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A Summary of Current Program, 7/1/62

and Preliminary Report of Progress

for 7/1/60 to 6/30/62

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SOUTHERN UTILIZATION RESEARCH AND

DEVELOPMENT DIVISION

of the

2 U.S. AGRICULTURAL RESEARCH SERVICE

UNITED STATES DEPARTMENT OF AGRICULTURE

This progress report of U.S.D.A. and cooperative research is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

There is included under each problem area in the report a brief and very general statement on the nature of the research being conducted by the State Agricultural Experiment Stations and the professional manpower being devoted by the State stations to such research. Also included is a brief description of related work conducted by private organizations. No details on progress of State station or industry research are included except as such work is cooperative with U.S.D.A.

The summaries of progress on U.S.D.A. and cooperative research include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed will be released promptly through established channels. Because of this, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a list of publications reporting results of U.S.D.A. and cooperative research issued between July 1, 1960, and June 30, 1962. Current agricultural research findings are also published in the monthly U.S.D.A. publication, Agricultural Research. This progress report was compiled in the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans 24, Louisiana.

UNITED STATES DEPARTMENT OF AGRICULTURE

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INTRODUCTION

The program of the Southern Utilization Research and Development Division is an organized effort through science and technology to increase present uses and to discover and develop varied new uses for Southern farm crops. Our farmers need new markets and strengthened demand for their production. At the same time, the Nation needs the new and better products that science can create from agricultural materials. To this end the Division conducts research on cotton, cottonseed, tung fruit, peanuts, rice, sugarcane, pine gum, citrus fruits, sweetpotatoes, cucumbers and other vegetables.

The Division's program includes basic and applied research in the physical and biological sciences and engineering. Basic research plays a key role in uncovering new information that may be later exploited in applied research and development. When appropriate, engineers carry out pilot-plant studies of promising laboratory developments to provide engineering and cost data essential to industrial application feasibility determinations. The Southern Division has a total staff of about 490, including 236 professional research scientists and engineers. The Division consists of 2 laboratories for pioneering research, 7 laboratories for research on specific commodities or groups of commodities, and 1 laboratory for engineering research and development. Headquarters of the Southern Division are located at the Southern Regional Research Laboratory, New Orleans, Louisiana. The Division also has personnel and laboratory facilities at Winter Haven and Olustee, Florida; Weslaco, Texas; Raleigh, North Carolina; Houma, Louisiana; and Natick, Massachusetts.

Division scientists consult with specialists from other organizations during both the planning and the execution of the research, and cooperate actively with industry to facilitate commercialization and utilization of new findings. Much of the cooperation is informal, but some work is conducted under conditions described in written cooperative agreements and memorandums of understanding. Currently 66 such agreements are in effect.

The farm products with which the Southern Division deals not only provide food, clothing and industrial raw materials, but also contribute to the Nation's general prosperity and well-being. Cotton, the Nation's number one cash crop, has an annual farm value of about \$2.5 billion. The retail value of cotton products is about \$18 billion. Cottonseed, a byproduct of cotton, has a farm value of around \$300 million. The retail value of its products is about \$2.4 billion. Citrus grown in the U. S. has a farm value of over \$500 million; vegetables over \$1 billion; peanuts over \$150 million; tung over \$7 million; and gum naval stores over \$20 million. The retail value of refined sugar produced from sugarcane grown in the United States and Puerto Rico is about \$600 million. Industries processing these agricultural crops play a vital role in the Nation's economy; agribusiness today is over 40% of the Nation's total economy.

There is an urgent need for utilization research to help maintain the traditional food, feed and industrial outlets for agricultural products and to create new and larger markets for them. Individual farmers cannot conduct utilization research, nor is there any organization of farmers that can support research of the scope or on the scale needed to be effective. Judging

by past experience, the ability of utilization research to benefit the economy is tremendous. In some cases, such as frozen concentrated orange juice, a research development is commercialized and in a relatively few years opens up an entirely new and profitable market for an agricultural commodity.

For the Southern Division the past two years was a period of continued improvement and significant achievements. Discoveries of a fundamental nature continued to lay the groundwork for later industrial breakthroughs in extending and improving the utilization of Southern farm crops. Commercialized developments continued to contribute directly to the Nation's economy. Some commercialized developments based on the research of Division scientists are summarized below:

High-stretch cotton fabrics opening new markets for cotton. The Agricultural Research Service has developed three methods for producing all-cotton knitted and woven fabrics with high recoverable stretch, durable loft, and increased warmth. These developments are viewed by industry as having potential benefits to cotton as great as the original development of a wash-wear cotton fabric. They should enable cotton to obtain a large share of markets that, within the next ten years, are expected to consume textile fibers in quantities equivalent to more than two million bales. Uses include upholstery, slip covers, industrial coated fabrics, bathing suits, dresses, hosiery, underwear, sweaters, sport shirts and many other uses where resilience and related properties are of importance to consumers. In one method fabrics are treated with a strong solution of caustic soda to impart the desired amount of stretch. In the other two methods cotton yarn is treated to impart high recoverable stretch, one involving a combination of resin and mechanical treatment and the other crimping yarns first made thermoplastic by chemical modification of the cellulose. At least two companies are in commercial production on the caustic treated fabrics, and a number of companies are producing products experimentally by the other two methods.

Practical method developed for imparting weather and rot resistance to cotton fabrics. A practical low cost treatment, developed for making cotton fabrics exposed to mildew, rot, and weathering last much longer, offers promise of maintaining a market of approximately 230,000 bales of cotton a year in canvas goods products such as awnings, tarpaulin, tentage, field coverings, beach umbrellas, ditch liners, and irrigation pipes. The treatment uses a chemical called "acid colloid of methylolmelamine", and can be applied with equipment already available in a great many textile finishing plants. One finisher has produced the colloid-treated fabric and supplied it to approximately six consumers who are using it as ditch liners, dam stops and in other applications. Other samples are under experimental exposure as seed bed covers in Florida.

New aerodynamic cleaner improves quality of cotton products. Developed as an attachment for the SRRL Opener and the Opener-Cleaner, the new SRRL Aerodynamic Cleaner is designed specifically to remove the motes and fine leaf (pepper) trash from cotton that are currently plaguing the textile industry. The cleaner has no moving parts and it processes cotton with a gentle action that

prevents fiber damage and neps. The machine became commercially available late in 1960 from several of the nine textile equipment manufacturers licensed under USDA's patents. The ability of the Air Cleaner to remove pepper trash caused by overmachining and overdrying during the ginning process will aid the textile industry to produce higher quality cotton products.

High quality cottonseed meal for feeding to poultry and swine.

It is estimated that between 250 and 500 thousand tons of cottonseed meal are being marketed yearly as a protein concentrate source for broiler rations. This new market for cottonseed meal is a direct result of cooperative research between Southern Utilization Research and Development Division, the National Cottonseed Products Association, State Experiment Stations and Industry in which improved processing techniques were developed to produce meals of lower gossypol content and high nutritional value. The new market in mixed feeds is particularly important since ruminants, the traditional market for cottonseed meal, do not require high quality protein and can be fed considerable amounts of synthetic nitrogen compounds such as urea. It is estimated that the present yearly value of the cottonseed meal going into these uses is \$22,500,000.

Acetoglycerides used commercially. It has been found that substituting acetic acid groups for some of the fatty acid groups in ordinary fats yields certain acetoglycerides having unique and valuable properties. One of these properties is the ability to remain quite plastic in the solid state. Acetoglycerides are being marketed in the United States and England for use in cosmetics. In July 1960, distilled acetylated monoglycerides up to 5 percent were approved by the Food and Drug Administration for such uses as (1) food coating agent, (2) a food container component, (3) an equipment lubricant, and (4) an emulsifier in foods. Licenses for the production of acetoglycerides under U. S. Patent No. 2,745,749 have been issued to several industrial concerns. The acetoglycerides could open up markets of more than 100 million pounds of domestic oils yearly. The value of such products could be more than \$50 million per annum.

Precooked, dehydrated sweetpotato flakes produced commercially.

Commercial production of precooked, dehydrated sweetpotato flakes -- a product developed by Division scientists in cooperation with the Eastern Division and the Quartermaster Food and Container Institute for the Armed Forces -- was initiated by one company during the 1961-62 season. The product is going primarily to institutional markets at the present time. Consumer acceptance tests on the flakes are in progress. Industry interest is high for the new product which can be reconstituted in 60 seconds and has the color and taste of freshly cooked mashed sweetpotatoes. It is expected that the flakes will open a profitable new market, especially for the substandard (odd sized and shaped) sweetpotatoes which now return little or no income to the farmer, and for the standard grades not absorbed by the demand for fresh, canned, and frozen products.

As these achievements indicate, utilization research is coming of age as a major force in nationwide efforts to maintain and expand markets for farm crops. The progress made during the past two years, and the exciting developments currently underway in the Southern Division, hold bright promise for a more prosperous agriculture and an improved economy.

* * * * *

In this report, there is presented a description of the Division's program as of July 1, 1962, and a summary of progress for the period July 1, 1960 through June 30, 1962. The Research and Marketing Advisory Committees, in their meetings during fiscal 1962, devoted their attention to a review of the research program of the Department, hence this report provides information on progress to cover the period since the last report on progress to the Committees.

AREA NO. 1 - COTTON - BASIC AND EXPLORATORY INVESTIGATIONS

Problem. Cotton, the nation's most important fiber, is facing severe and increasing competition from synthetic fibers. Cotton is America's largest source of cash farm income and still accounts for almost two-thirds of the total U. S. mill consumption of all major fibers. However, its proportionate share of the market has been slowly decreasing as has the per capita consumption. The rapid growth of the synthetics at the expense of the natural fibers has been a phenomenon of the century. Expansion of market outlets for the chemical fibers has been based on vigorous research and development programs. The engineering and development programs of the chemical fiber industry are designed to capitalize on the special properties of each individual fiber as related to the functional use qualities desired in particular products; basically they involve the substitution of the newer fibers for cotton in cotton's traditional end use markets. Expanded research to increase the utilization potential of cotton offers the most realistic opportunity for improving cotton's competitive strength as a textile fiber and for increasing cotton consumption. Basic and exploratory investigations, studies on interrelations among fiber, yarn, and fabric properties, new and improved textile machinery, improvement of wash-wear properties and improved cotton properties and products are basic to holding existing markets or expanding the use of cotton in new applications.

Fundamental information is badly needed in applied research to help cotton gain new and maintain old markets. Fundamental knowledge of the cotton fiber as to its structure, properties, and the mechanisms involved in chemical and physical behavior serves as a basis and a guide in the design and improvement of processing machinery, mechanical and chemical processes, and in the development of new and improved cotton yarns, fabrics, finishes, and treatments. Many chemical and physical treatments, as well as textile organizations and machine designs, offer a basis for the improvement of cotton quality or lowering of processing costs. Expanded exploratory chemical and physical research is needed to determine the true potential of such approaches prior to undertaking extensive developmental research or the construction of prototype machinery. Specific areas in which basic information is needed include the chemical properties and structure of native and modified cottons; the chemical modification of cotton cellulose; chemical reactions induced in cotton cellulose by high energy radiation; application of tagged elements to studies of native and modified cotton cellulose; reaction mechanisms, rates, and catalysis of cotton cellulose reactions; new concepts and methods for evaluating the physical properties of native and modified cottons; relationships of the structural arrangements within cotton fibers to the physical properties of native and modified cottons; mechanisms of physical damage to cotton due to mechanical, chemical, or biological actions; fine structural changes occurring during chemical and physical modification of cotton cellulose; and correlations of the fine structure of cotton fibers with their gross behavior in textile structures.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists, analytical chemists, physical chemists, physicists, microscopists, chemical engineers, statisticians, mathematicians, cotton technologists and textile technologists engaged in basic and exploratory studies to develop fundamental information needed in applied research to help cotton gain new and maintain

old markets. Basic research on the structure of cotton fiber and its relation to the behavior in mechanical and chemical treatments, essential to an understanding of the performance of fibers during processing and in textile products, is carried out at New Orleans, Louisiana. Exploratory chemical and physical research is also conducted at New Orleans, Louisiana, as a basis for the improvement of mechanical and chemical processing, and in the development of new and improved yarns, fabrics, finishes, and treatments. Additional exploratory chemical and physical investigations are being carried out under contract at the Textile Research Institute, Princeton, New Jersey, on the investigation of non-aqueous swelling agents for cellulose to provide new chemical and physical modifications of cotton; and at the Massachusetts Institute of Technology, Cambridge, Massachusetts on the mechanics of nep formation in cotton during processing.

Other research on chemical and physical properties and structure of cotton is in progress under grants of P.L. 480 funds to the following foreign institutions: Ministry of Commerce and Industry, Jerusalem, Israel, for fundamental investigation of crimp in cotton fibers and its relationship to other fiber properties (5.0 professional man-years); National Institute of Applied Chemical Research, Paris, France, for a fundamental study of the relation of crystallinity to accessibility in cottons (4.3 professional man-years); Swedish Institute for Textile Research, Goteburg, Sweden, for an investigation of setting reactions in cotton fabrics (2.0 professional man-years); Central Organization for Applied Research, T.N.O., Delft, Holland, for a fundamental study of the response of cotton fiber structural elements to stress (1.0 professional man-years); Shirley Institute, Manchester, England, for a fundamental study of the microbiological breakdown of cotton fiber (4.5 professional man-years); and University of Bombay, Bombay, India, for an investigation of the photochemical degradation of cotton (3.3 professional man-years). Exploratory chemical and physical investigations are in progress under grants of P.L. 480 funds to the following foreign institutions: Shirley Institute, Manchester, England, for a fundamental study of the pyrolysis of cotton cellulose (4.7 professional man-years); Ministry of Commerce and Industry, Jerusalem, Israel, for a study of the effect on cotton of oxidizing agents (3.0 professional man-years); and University of London, London, England, for a fundamental investigation of preparation and properties of phosphonitrilic derivatives for use in treating cotton (4.0 professional man-years).

The Federal in-house scientific effort devoted to research in this area totals 44.5 professional man-years. Of this number 23.3 is devoted to chemical and physical properties and structure and 21.2 to exploratory chemical and physical investigations. The contract research involves an additional 2.6 man-years, all of the effort being on exploratory chemical and physical investigations. P.L. 480 research totals 31.8 man-years, of which 20.1 is on chemical and physical properties and structure and 11.7 is on exploratory chemical and physical investigations.

The following lines of work were terminated during the year: (1) Investigation of the effect of fiber drag on the draftability of cottons (under chemical and physical properties and structure); and (2) Study of influence of cotton fiber properties and atmospheric conditions on nep formation. (3) Systematic investigation of non-aqueous swelling agents for cellulose. (4) Treatment of cotton with gamma radiation and chemicals to develop improved cotton products (under exploratory chemical and physical investigations).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 0.5 professional man-year effort in this area, all of which was under the subheading chemical and physical properties and structure. The investigations involve evaluation of cotton varieties grown in different locations in the state, in different seasons and under various production treatments, for important fiber qualities such as fineness, elongation and strength.

Industry and other organizations conduct little research in this area. The cotton industry and textile schools do a small amount (estimated 4 professional man-years per year) of fundamental or exploratory work on physical or chemical properties or structure of cotton. Some chemical companies conduct a limited amount of basic research on physical and chemical properties to develop necessary information required to guide their efforts, but, in general, their endeavor in this area is devoted to screening their own chemicals for possible application to cotton. Their estimated annual expenditures in the basic and purely exploratory field in the same areas as the federal research are equivalent to approximately 3 professional man-years.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical and Physical Properties and Structure

1. Application of Radioactively Labeled Reagents to Studies of Native and Modified Cottons. Radioactively labeled celluloses provide a unique means for investigation of the mechanisms of selected chemical and radiation chemical reactions involving chemically modified cellulose. In recent research a closed system for the semi-micromethylation of cellulose, in which the excess of radioactively tagged methylating agent is recovered, has been developed. Tagged methyl celluloses with different degrees of substitution (D.S.) are being prepared for use in investigating the radiation chemistry of methyl cellulose. (S2 1-151).

2. Studies of New Concepts and Methods for Evaluating the Physical Properties of Native and Modified Cottons. Exploratory research was initiated to evaluate the swelling behavior of cotton fibers in various environments by observation of the untwisting of single yarns. Microscopical measurements of the swelling of fibers in selected liquids are being correlated with the untwisting rate of mercerized and of grey yarns in these reagents; and with imbibition results by the centrifuge method of Rebenfeld. The untwisting technique offers promise as the basis for a rapid and simple method for evaluation of swelling behavior of cotton in the solutions used in various pretreatments before chemical modification or crosslinking, or in the environments in which these reactions are carried out. Correlation of results of several methods of estimating swelling with the rate of untwisting of cotton yarns will be sought and classification of reagents into several categories on the basis of these results will be attempted. (S2 1-182).

3. Basic Studies of the Relationships of the Structural Arrangements Within Cotton Fibers to the Physical Properties of Native and Modified Cottons. Research was continued on the microfibrillate structure of cotton and other cellulosic fibers. Using the mathematical extrapolation of Sippel, intrinsic tenacity values for cotton, flax and ramie were determined. At extremely short test lengths, the tenacities of cellulosic fibers approach the theoretical

maximum value. The research indicates that the elimination or decrease in the frequency of weak regions along the cotton fiber length could improve the strength properties of cotton. This work may prove of value in cotton breeding work.

Light and electron microscopy are being employed to study the character, location, and distribution of regions of reacted cellulose and unbound additive substances in chemically treated cotton fibers as a means of investigating the mode of chemical modification.

Microscopical evaluation of the effects of various crosslinking agents have confirmed that temperature and type of catalyst play an important role in the degree of crosslinking. Electron microscope observations of swelling patterns of ultrathin sections of cotton fibers in 0.5 M cupriethylenediamine indicate that when formaldehyde is used as the agent, crosslinking is a function of both catalyst and temperature. Observations of samples treated at 160°C. (dry cure) with 1.65% or 3.3% formaldehyde in the presence of $\text{Zn}(\text{NO}_3)_2$, MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, or ZnCl_2 indicate best crosslinking when $\text{Zn}(\text{NO}_3)_2$ is the catalyst, but little or no crosslinking was obtained with any of these catalysts when the fibers were treated with 3.3% formaldehyde at 45°C.

In future work ultrathin sections of cotton fibers under various chemical reaction conditions will be observed, and the effect of selective solvents on reacted and nonreacted areas evaluated. The development of electron microscope methodology for evaluation of crosslinking, substitution and other modes of altering the properties of cotton will provide a potent tool for eventual prediction of the ultimate usefulness of reagents and processes proposed for the treatment of cotton. (S2 1-174).

4. Elucidation of Mechanisms of Physical Damage to Cotton Due to Mechanical, Chemical, or Biological Actions. Microscopical comparisons of various types of abrasion on untreated and treated cotton has provided basic information for the better understanding of mechanisms involved in the abrasion of cotton fibers. Light and electron microscopical techniques developed for appraisal of damage at the fiber and subfiber levels permit more detailed study of phenomena involved. It is evident that abrasion resistance treatments must be evaluated under wet as well as dry conditions in testing. Surfaces of dry-flexed fibers are smooth, whereas those of wet-flexed fibers are much disturbed by peeling back of fiber wall layers. In contrast to flex abrasion, damage in flat abrasion is by gouging out jagged fragments of several layers of fiber wall. These findings should contribute toward potential improvement of abrasion-resistant treatments.

Further progress was made in determining the microscopical changes occurring in the fibrillar structure of native and modified cottons upon degradation by various agents. This information is basic to an understanding of factors responsible for shortened service life of textile products. Microscopical studies have shown that cotton fiber degradation by hydrolytic agents and by oxidation appears to result ultimately in rupture of the cellulose chains. Transverse breakdown of cotton cellulose microfibrils through the action of oxidizing agent (periodate) has been found to lead to increased accessibility to water and lower crystallinity, whereas acid degradation shows the opposite effect. Fibrillar swelling is more closely related to an increase in carboxyl content than to changes in amorphous content. Acetylation and crosslinking appear to cause increased thickness of the fibrillar fragments. Correlation

of microscopically observed changes in microfibrillar pattern with data from chemical analyses may serve to enhance appreciation of the effects involved. (S2 1-152).

Fundamental studies of the microbiological breakdown of cotton are being conducted at the Shirley Institute under the P.L. 480 research program. Cotton fabrics in many applications are exposed to bacteriological and fungicidal attack. Studies of the enzyme systems involved have shown that these systems consist of at least two types. One of these, less of which is present in isolated enzyme preparations, appears to penetrate the cellulose more readily, thus accounting for the significantly greater degradation of cotton caused by living organisms. Progress has been made toward the isolation and determination of the molecular properties of the enzyme system involved. (UR-E29-(20)-6).

5. Investigation of the Fine Structural Changes Occuring During Chemical and Physical Modification of Cotton Cellulose. The infrared absorption spectra of native, degraded and chemically modified cottons are being investigated as a means of elucidation of structural and chemical changes due to chemical treatment. Infrared studies on deuterated fibers have brought out several interesting facts about the behavior of amorphous and crystalline cellulose, which may be significant in the further study of the molecular structure of the cotton fiber as an aid to determining the nature of the reactions of cotton with various modifying reagents. Considerable attention has been given to the development of a "differential" technique, in which the infrared spectrum of cotton is "subtracted" from that of a cotton derivative by means of the double-beam spectrophotometer. This technique has been successful in intensifying absorption bands in certain cotton derivatives which previously had been largely masked by the bands present in cotton itself. It also enhances the linear scale expansion of spectra for observing and resolving bands which may be overlooked by ordinary methods.

Infrared absorption bands suitable for quantitative estimation of the functional groups in several important cotton modifications have been established. These include the reaction products of cotton with the methylol compounds of urea, ethyleneurea, ethyl triazone, melamine, uron, and ethyl carbamate. The limits of the analyses by this method are considerably lower than the quantities applied for producing wash-wear characteristics in cotton. The products extracted from cotton derivatives of current interest by treatment with dilute mineral acids and strongly polar organic solvents will be studied by infrared spectroscopy. The results of these observations should permit more definite conclusions to be drawn about the chemical nature of the cellulose derivatives. (S2 1-165).

Pioneering research on plant fibers has been directed along two principal lines: (a) to analyze and interpret the nature of the fine structure present in plant fibers with emphasis on cotton; and (b) to interpret the changes in the fine structure induced by various chemical modifications of cellulose such as introduction of bulky or sterically hindered ester or ether groups, amine complexing agents and swelling compounds. Since the previous investigations under (a) have been quite extensive, major recent effort has been in the field indicated by (b).

With the aid of a graded series of alkali concentrations from 2 to 18% sodium hydroxide, moisture sorptive, X-ray diffraction and infrared measurements and with hydrogen-deuterium exchange applied to cotton fibers from 10 to 50

days old, it was shown that the cellulose structure changes greatly during growth. Not only does the accessibility undergo a rather remarkable change, but the average degree of lateral order of the crystalline cellulose as well as its heterogeneity apparently increase significantly during development.

Other studies relating to fine structure of unmodified cellulose have had to do with the infrared spectra of cellulose I (native) and cellulose II (mercerized). It was found that three new absorption bands, not previously used, were related to the crystallinity of both polymorphic forms of cellulose. They differed in this respect from the previous infrared "crystallinity index" which was applicable only to cellulose I. The suitability of these new bands for crystallinity assay is being explored.

Under research on chemically modified fibers, a dozen or more new cellulose esters and ethers have been prepared for the first time by heterogeneous reactions with retention of the fibrous structure. These have been partially evaluated by physical and chemical methods. Some of the esters are sterically hindered and almost completely resistant to alkali splitting. In some of the derivatives which have been studied the rates of formation or saponification were consistent with a diffusion-controlled reaction kinetics.

In the case of benzhydryl celluloses, one of the new cellulose derivatives, it has proved very difficult to substitute more than about one third of the available anhydroglucose units of the cellulose. Furthermore, at this stage the crystalline structure of the cellulose has decreased somewhat and changed to that of the benzhydryl cellulose. Considerable indirect evidence suggests that nearly all of the substitution occurs in the primary hydroxyl position, but some evidence indicates a small amount of substitution occurs at a secondary hydroxyl.

The modifications of cellulose structure, brought about by complexing of the cellulose with amines, have been investigated along two principal lines: (1) a better characterization of the various amine complexes; and (2) the residual reactivity of the amine with amine reactive substances. Under the first category such cellulose complexes as those with ethylamine, ethylenediamine, hexamethylenediamine, diethylenetriamine and allylamine have been more fully characterized and the conditions of their formation clarified. As a general rule the secondary amines do not complex with cellulose.

In order to learn something of the reactivity of the complexed amine it was necessary generally to employ nonaqueous media to avoid destruction of the complex by water. Among reactants studied were sebacyl chloride, butanedione (tetramethyl-1,3-cyclobutanedione), divinyl sulfone and ethylenimine. Such nonaqueous media as carbon tetrachloride, benzene, etc. were used. In some cases the complex restricted the activity of the amine, in others, not. In several cases polymers of the reactant were deposited on or in the cellulose.

Of the four polymorphic forms of cellulose only cellulose II has been artificially prepared in crystalline form thus far. This was accomplished by other investigators by first preparing the crystalline triacetate and saponifying it in heterogeneous state. An attempt is being made in the current research to prepare cellulose I in crystalline form.

In spite of the large amount of work that has been done on thermoplastics, practically no research findings have been published on thermoplastic textile

fibers. A means of measuring thermoplasticity in chemically modified cellulose fibers has been worked out and applied to acetylated cotton. The conditions of degree of substitution, temperature, plasticizer (steam) and other factors important in the thermoplastic behavior of acetylated cotton have been established.

In highly acetylated cotton cellulose the original crystal structure of the cellulose has been nearly if not completely destroyed and, unless heated, the new crystal structure of the triacetate does not develop. Temperatures of 175-225°C., however, cause extensive crystallization. It now has been established that certain organic liquids, such as dimethylformamide, chloroform, acrylonitrile, formic acid and others, will cause partial crystallization at room temperature. Some cause cellulose triacetate I to form, some the triacetate II. Surprisingly, cellulose triacetate II reverted to cellulose I when saponified in the presence of sodium acetate.

In order to identify and characterize the changes in fine structure induced in cotton cellulose by chemical modification, the process of acetylation was chosen and applied to scoured cotton yarn by two acetylation techniques to give a range of degrees of substitution from DS = 0.78 to 2.93. Reaction proceeded in harmony with the Sakurada diffusion-controlled kinetics. Changes in crystalline structure, and tensile properties were followed at various temperatures up to 230°C. Density decreased progressively with acetylation. Crystallization of the triacetate occurs at substitutions of DS = 1.5 or greater and at temperatures of 175-225°C. Thermal studies disclosed a plastic region in the unheated products between 125 and 175°C. A glass-rubber transition occurs at 180-190°C. in the amorphous component of the partially crystalline structure and strongly influences such properties as tensile stiffness, and elastic and work recovery in these temperature ranges. Studies of structure in both native and chemically modified plant fibers are continuing.

In P.L. 480 research at the National Institute of Applied Chemical Research, a basic study of the fine structure of the cotton fiber is being conducted in an effort to relate the fine structure to other fiber properties that are important in the processing and use of cotton. Improved methods, both physical and chemical, have been devised for measuring differences in the fine structure of cottons. These are being applied to a typical U. S. cotton of Deltapine variety, the fiber properties of which have been extensively studied in several laboratories, and are thoroughly known. Similar studies are being made of a series of raw, purified, and chemically crosslinked cotton yarns. The information obtained eventually will be translated into the development of improved cotton products. (UR-E9-(20)-61).

6. Correlations of Cotton Fiber Structure With Gross Behavior of the Fibers in Textile Structures. Fiber drag embodies such physical properties as surface friction, rigidity, crimp, and elongation. Research has been directed toward measuring and determining the effect that fiber drag has upon draftability of cottons to improve processing techniques and quality of yarns. Static (Instron) and dynamic (West Point Cohesion Tester) methods of determining drag gave similar rankings to the different cottons tested. For both methods, it was necessary to test at several test lengths to determine the drag characteristics of a cotton. Equations relating test length to breaking and drafting tenacity, respectively, for the static and dynamic methods were developed. The dynamic method showed that at short test lengths, fiber length and strength appeared to be the critical fiber properties affecting drag,

while at longer test lengths fiber fineness was the critical property. Increases in length, strength, and fiber size increased fiber drag.

It was found that when fibers were treated with selected chemical additives (colloidal silica and colloidal alumina), large increases in drag were produced. However, large reductions in fiber drag were not obtained when lubricating chemicals were applied. A fairly rapid and reliable method of determining fiber arrangement, especially hooked fibers, was developed. It was established that card sliver hooks are more easily removed in drafting in the trailing position than in the leading position. Thus processing efficiency can be increased by changing processing techniques to put more emphasis on drafting card sliver hooks in the trailing direction. (S2 1-160).

A fundamental investigation of fiber crimp, a property possibly responsible for differences in mechanical processing behavior of cotton fibers, is in progress under P.L. 480 research at the Ministry of Commerce and Industry of the State of Israel. An optical projection system has been developed to measure crimp in two perpendicular planes. The main crimp parameter is crimp-diameter, an average crimp amplitude for fiber in a static position. Crimp-diameter decreased with tension for Deltapine 15 fibers. When energy required to uncrimp fibers was measured, that for Deltapine fibers remained essentially constant after the first stretching cycle. Energy for Acala 1517 fibers decreased with the first through fourth stretching cycles and increased with period of relaxation, a distinct difference in behavior of these two cottons. Techniques for evaluating fiber crimp are being improved and applied to a number of cottons of differing physical characteristics. (UR-A10-(20)-5).

B. Exploratory Chemical and Physical Investigations

1. Exploratory Chemical Modification of Cotton Cellulose. In exploratory research involving investigations of chemical reactions for attaching reactive compounds to cotton by means of formaldehyde and other polyfunctional reagents, it has been demonstrated that finished garments can be made wrinkle resistant by a novel vapor phase formaldehyde treatment. Vapors from paraformaldehyde mixed with volatile acid catalysts are employed. This vapor phase process may be used in binding to cotton a variety of active hydrogen compounds, amides, polyamides, phosphoramides, alcohols and phenols. These compounds impart to cotton a number of useful properties, such as wet and dry crease recovery, flame resistance, and starched appearance. The vapor method is convenient, versatile and effective for experimental treatment of cotton.

A new method of attachment of starch or of polyvinyl alcohol to cotton fabric with divinyl sulfone has been found, utilizing a solution composed of sodium bicarbonate, starch, and sulfone. Improved crease recovery has been obtained in this manner. Ethylene glycol and sorbitol have been successfully attached to cotton fabrics by means of vapor from HCl-paraformaldehyde. The elongation at break, flex abrasion, moisture regain and wet crease recovery of fabrics treated in this way were appreciably higher than obtained with HCl-paraformaldehyde alone. Dihalogen compounds, including dichloroacetic acid, have also been shown to be useful in crosslinking cotton cellulose and introducing new functional groups at the same time. New crosslinking agents for cotton, chloroacrylic and dichloropropionic acids, have been found. These crosslinkers introduce carboxyl groups into the cellulose molecule at the same time, and may prove useful in special applications.

A variety of formaldehyde-reactive monomers and polymers, such as amides, alcohols, thiols, and phenols, have been bound to cotton cellulose by either the formaldehyde vapor phase method or wet methods. The incorporation of dyes and stiffeners into cotton cellulose by either method appears to offer a convenient experimental treatment for cotton fabrics and possibly finished garments. An important problem in the commercial application of bis(hydroxyethyl) sulfone to cotton, yellowing caused by heat curing, has possibly been solved by use of traces of sodium borohydride together with a fluorescent whitener. This research will be continued with emphasis on the investigation of other catalysts and treatment methods to determine if the fabric strength of cotton treated with formaldehyde or other polyfunctional compounds can be improved. (S2 1-161, S2 1-186).

Chemical pretreatments of cotton are being explored as a means of improving the physical properties of chemically modified cotton textiles. Emphasis is on the production of resilient cotton textiles having improved tensile and tear strength. In experiments with cotton yarn, it was discovered that pretreatment of the yarn with trimethyl phosphite prior to chemical modification of the cotton activates the cotton for reaction with arylisocyanates and has the unexpected dividend of increasing breaking strength. Slack mercerization of yarn and subsequent tensioning prior to resin treatment with dimethylol ethyleneurea (DMEU) more than offsets the breaking strength loss normally observed during the crosslinking. Strength gains were largest if the mercerization was at low temperature. The belief that crosslinking of cotton inevitably causes an overall loss of strength is incorrect. Likewise, increased elastic properties were shown to be compatible with the crosslinking of cotton, when acid pretreatments (such as 71% nitric acid) were applied prior to DMEU resin finishing.

Yarn which has been slack mercerized and restretched may be woven into a fabric which, on subsequently being crosslinked, has as high a breaking strength as uncrosslinked fabric woven with untreated yarn. The new fabric possessed moderate wrinkle resistance. A fabric having fair wash-wear properties, considerable stretch, and little strength loss was made by the "Form W" formaldehyde process followed by slack mercerization. In future work pretreatments of yarn from which a fabric is woven will be compared and also combined with pre- and after-treatments applied to the crosslinked fabric, for their effect on strength, extensibility and abrasion resistance. (S2 1-167).

A study is being made of the factors that influence the development of thermoplastic properties in cotton to provide information for developing new types of cotton products. Thermoplasticity is needed for easy garment fabrication, for pleating, embossing, and creasing of special garments, and for production of stretch cottons.

Due to their chemical stability, emphasis in the research is on the production of etherified cottons having thermoplastic characteristics as well as resilience. Thermoplastic partially acetylated cotton yarns have been prepared, crimped by the Helanca process, and then knitted to produce more bulky cotton textiles with stretch. In studies on an etherified cotton, benzylated cotton, a method has been developed for the uniform benzylation of fabric in amounts needed for determination of physical properties. Cotton yarns have also been benzylated to high degrees of substitution (up to D.S. of 1.7) for study of their thermoplastic properties. The discovery of an accelerator for the benzylation of cotton should make this method of preparing thermoplastic cotton

more economical than in the past. The high strength retention obtained in allylation and benzylation shows that these are usable methods of imparting thermoplasticity to cotton.

A false twist has been imparted to cotton yarn by swelling the latter for a few minutes in 40% aqueous benzyltrimethyl-ammonium hydroxide, coiling the yarn under tension and deswelling the coiled yarn in boiling water. This method has been used to impart considerable stretch to cotton yarn. The types of chemical reagents that will induce plasticity in cotton without causing substitution of the cellulose will be studied, and applications to yarn and fabric finishing determined. (S2 1-172).

In addition to increasing the fundamental knowledge of crosslinking of cotton cellulose, investigations in progress on the breaking and reforming of cellulosic crosslinks in cotton fabric may lead to processes that impart permanent creases or pleats in wrinkle resistant wash-wear cotton fabrics.

Dialdehyde cotton forms weak crosslinks capable of being broken and reformed, but it is not suitable for textile use because of its sensitivity to alkaline solutions. By reducing dialdehyde cotton to dialcohol cotton, then tension-mercerizing the cotton, up to 100 percent increase in strength has been obtained. This could have an application of industrial value when used as an activating pretreatment for chemical finishing processes.

A compound (β, β' -Dichlorodiethyldisulfide) was found for introducing a disulfide crosslink into cotton cellulose capable of being broken and reformed. Unfortunately, the crosslink is unstable to repeated processes of breaking and reforming the linkage. However, two promising new methods for incorporating mercapto groups into cotton fabric have been explored: (1) mercapto-ethylating cotton with ethylene sulfide, (2) reaction of dialdehyde cotton with hydrogen sulfide.

Strong evidence has been obtained for the presence of disulfide crosslinks in ethylene sulfide-treated cotton after it has been oxidized with iodine. The objective of introducing into cotton cellulose crosslinks which can be broken and reformed by mild oxidation and reduction appears to be close to realization. Study of the sulphydrylation of cotton through dialdehyde cotton or mercapto-alkylation will continue. Increasing the extent of disulfide crosslink formation to obtain greater fabric property changes will be emphasized. (S2 1-168).

Fundamental investigations of the reaction of cotton with epoxy compounds is leading to a better understanding and improvement in efficiency of these reactions. Data on rates of hydrolysis of the oxirane rings of these compounds have indicated differences in ring opening with difference in structure. By removal of the proper amount of moisture from cotton prior to reacting it with diepoxide finishing agents, dry crease resistance has been imparted to the cotton at low add-ons. It has also been established that removal of too much water results in no reaction with the diepoxides.

The use of diepoxide precursors, such as the dihydrohalogens, in place of the diepoxides has been shown to be feasible. Several dihydrohalides, which are the precursors of the d,l- and meso butadiene diepoxides, have been reacted with cotton cellulose in the presence of alcoholic sodium hydroxide. The d,l-butadiene epoxide has been reacted with cotton in the presence of strong aqueous sodium hydroxide solutions. In contrast to fabrics finished with the

meso isomer, these products possessed excellent dry and wet crease resistance at relatively low add-ons. More efficient processes will be sought for attainment of the desired properties imparted by the d,l isomers of butadiene diepoxide, and experimental evidence will be accumulated to be used for the elucidation of the cellulose-butadiene diepoxide reaction mechanism. (S2 1-169).

In contract research at the Textile Research Institute, a systematic investigation has been conducted on the use of non-aqueous swelling agents for increasing the chemical reactivity of cotton cellulose, as well as enhancing its receptivity to physical modifications. Results clearly indicate that certain organic systems have the ability to penetrate cotton and to cause disruption of its native hydrogen bonded structure without impairment of the fiber mechanical properties, thus making feasible many new cotton modifications. In binary systems consisting of non-aqueous solvents which are not imbibed, the significant dependence of imbibition values upon solute concentration indicates "compound" formation with such compounds having characteristic swelling power. Low level formylation followed by removal of the formyl group results in a cotton of higher accessibility and represents a general method for increasing cotton cellulose reactivity. The imbibition of cyclohexanone by cellulose indicates an interaction between the six-membered cyclohexanone ring and the six-membered glucopyranose ring and suggests the importance of considering molecular configuration and conformation as well as the functionality of the organic reagent used in preswelling treatments. (S2 1-158(C)).

In P.L. 480 research at the University of London, the preparation and properties of phosphonitrilic derivatives for use in treating cotton are being investigated. Phosphorous compounds of certain structures are known to confer highly desirable properties such as flame resistance and improved resilience to cotton. The exploratory research in progress is on derivatives of the phosphonitrilic chlorides. New knowledge has been developed on the effect of structure on the reactions and properties of specific classes of phosphorous compounds which makes possible the preparation of specially designed reagents for the chemical modification of cotton. Some of these are being prepared in quantities sufficient for testing on textiles. (UR-E29-(20)-35).

2. Chemical Reactions Induced in Cotton Cellulose and Chemically Modified Cotton by High Energy Radiation. A radiation-induced grafting reaction of cotton cellulose has been demonstrated. Through this fundamental research, ways have been indicated to modify cotton chemically and to add unusually large quantities of acrylonitrile to cotton yarn without losing its textile properties. Cyanoethylation of cotton up to a degree of substitution of 0.7 permitted subsequent gamma-radiation polymerization of acrylonitrile onto cyanoethylated yarn at dosages of 1 megareoentgen without loss in the physical appearance of the yarn. Increased elongation-at-break and decreased stiffness were obtained, accompanied by only slight losses in breaking strength.

The reactions of high-energy radiation activated and chemically modified cotton cellulose were investigated. The presence of long-lived activated molecular species (probably free radicals) in the high-energy gamma irradiated cotton cellulose was indicated (1) by post-irradiation changes in the molecular properties of the cellulose, and (2) by post-irradiation reaction of cellulose with acrylonitrile. Irradiated cellulose, on standing, depolymerized slightly (as determined by intrinsic viscosity). There was no post-irradiation change in the tensile strength of the irradiated cotton. Irradiated cotton reacted with acrylonitrile to yield graft polymers. The use

of radiation activation to induce crosslinks in chemically modified cellulose was shown on the irradiation of methyl cellulose. When water-soluble methyl cellulose was irradiated, a water-insoluble gel was formed, indicating radiation-induced crosslinks. Irradiation of methylated cotton yarns (low methoxyl content) gave no indication of crosslinking, as determined by the elastic recovery properties of the irradiated yarns.

In recent research, cotton yarns containing polystyrene and polyacrylonitrile and possessing thermoplastic properties have been made by a high energy radiation process. The process involves use of high energy gamma radiation to initiate polymerization of the vinyl monomers onto the cotton. Further studies on the post-irradiation polymerization reactions of vinyl monomers and cotton and an evaluation of the textile properties of the products will be carried out. (S2 1-159; S2 1-176).

3. Basic Investigation of Reaction Mechanisms, Rates and Catalysis of Cotton Cellulose Reactions. P. L. 480 research at the Shirley Institute on the pyrolysis of cotton cellulose is continuing to provide information needed for improvement of flame-resistant treatments for cotton. Reduced flammability of cotton textiles for apparel, draperies, awnings, etc., is highly desirable from the standpoint of safety. The nature of the reactions involved in the burning of cotton is such that the first products of pyrolysis (oxygen-containing materials such as tars, carbon monoxide, etc.) require little outside oxygen for further combustion. It has been demonstrated that the degree of flame resistance of cotton fabrics is related to the char to tar ratio upon pyrolysis. Hence, finishes to reduce the flammability of cotton should be directed at altering the sequence of the reactions involved. (UR-E29-(20)-9).

Good progress has been made in P.L. 480 research at the Ministry of Commerce and Industry of the State of Israel on a fundamental study of the oxidation of cotton by various oxidizing agents to obtain data on the kinetics of the oxidation and the changes in physical and chemical properties which occur. Hypochlorite is widely used in the finishing of cotton textiles. Basic investigations of oxidation of cotton with hypochlorite, the common commercial and home bleaching agent, have explained the mechanism of the degradation which occurs. The results of this research indicate oxidation and resulting breakdown is random and involves both cleavage of the cellulose polymer chain followed by oxidative attack at these points. These degradative changes are a function of oxygen consumption rather than the pH of oxidation. (UR-A10-(20)-4).

4. Exploratory Physical Investigations on Cotton. Encouraging progress has been made in contract research at the Massachusetts Institute of Technology to determine the mechanics of nep formation in cotton during textile mechanical processing. An impressive statistical analysis of published literature relating fiber properties to neps has been completed. Hitherto unsuspected relationships between neps, fiber properties, and the behavior of fibers during processing are indicated which, if verified, should prove valuable in cotton breeding and processing research. The effects of staple length, Pressley strength, and Causticaire maturity index on nep formation are negligible. The number of neps formed during processing was closely related to the Micronaire readings of the cotton samples studied. Theoretical studies will be extended to consider fiber curling versus mechanical properties of the fiber. Fiber behavior during carding and under impact loading will be

investigated. (S2 1-173(C)).

Initial work involving fundamental investigations of the drying of chemically modified cotton has resulted in development of a procedure for precise measurement of drying rates utilizing an Instron strain gage to continuously record the change in weight. Preliminary experiments indicate the presence of two previously unreported drying phenomena. Data obtained on rate of drying of a series of acetylated cottons varying in acetyl content is currently being computed preparatory to interpretation of the results. The research may prove valuable not only in improving commercial drying techniques but also in obtaining greater knowledge about the chemically modified cottons and fiber structure. (S2 1-188).

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AREA NO. 2 - COTTON - INTERRELATIONS
AMONG FIBER, YARN, AND FABRIC PROPERTIES

Problem. The intense competition in today's textile markets is placing increasing demands upon cotton producers and processors for high quality products tailored to meet specific use requirements. Improvement in the quality of processed products and lower costs of mechanically processing cotton into yarns and fabrics are needed to satisfy consumer demands and maintain cotton markets. For example, information is needed to determine the effect of the important fiber properties and combination of fiber properties of cottons on yarn and fabric properties and processing performance to obtain the maximum utilization potential from cottons of different fiber properties and to provide guidance for cotton breeders in developing strains having more desirable fiber properties. Improved mechanical processing methods are needed to attain maximum yarn uniformity and the resultant improvements in the general quality level and processing efficiency of all types of cotton products. New and improved methods and instruments for measuring the physical and chemical properties of cotton are needed to guide processing research in developing new and improved products.

USDA PROGRAM

The Department has a continuing long-term program involving cotton technologists, textile technologists, textile engineers, physicists, statisticians, and mathematicians engaged in research to develop fundamental information and improved processing procedures in order to improve the quality and lower the cost of cotton products during the mechanical processing of cotton fibers into yarns and fabrics. Research to determine the effect of fiber properties on processing efficiency and product quality is carried out at New Orleans, La. Additional research of this type is conducted under contract at Auburn Research Foundation, Inc., Auburn, Alabama, involving large-scale spinning evaluations of the effect of fiber properties and spinning variables on yarn properties and end breakage. Cooperation is maintained with cotton merchants and textile mills; the Crops Research Division, specially on the procurement of cotton of known history with special fiber properties; and the Market Quality Research Division, AMS, to insure coordination of effort in related research. Research on development of new and improved methods and instruments for measuring the physical and chemical properties of cotton, and evaluating the processing characteristics of cotton, is carried out at New Orleans, Louisiana.

Other research on effect of fiber properties on processing efficiency and product quality is in progress under grants of P.L. 480 funds to the following foreign institutions: Shirley Institute, Manchester, England, for a fundamental investigation of the causes of warp breakage in the weaving of cotton yarns (3.2 professional man-years); and Juan de la Cierva School of Technical Investigations, Barcelona, Spain, for an investigation of the relationship between the cohesion of cotton fibers and the properties of rovings and yarns (2.5 professional man-years), and for an investigation of the effect of drafting force on cotton yarn strength and uniformity (2.0 professional man-years). Research on development of new and improved methods and instruments for measuring physical properties of cotton is in progress under grants of P.L. 480 funds to the following institutions: Juan de la Cierva School of Technical Investigations, Barcelona, Spain, for the development of methods and equipment for determining irregularity of transparency of card web and for counting neps (2.5 professional

man-years); and German Research Institute for Textile Industry, Reutlingen-Stuttgart, West Germany, for the development of an apparatus for counting neps in cotton card web (2.3 professional man-years).

The Federal in-house scientific effort devoted to research in this area totals 11.3 professional man-years. Of this number 9.5 is devoted to investigations of effect of fiber properties on processing efficiency and product quality and 1.8 to development of new and improved methods and instruments for measuring the physical and chemical properties of cotton. The contract research involves an additional 1.0 man-years, all of the effort being on investigation of effect of fiber properties on processing efficiency and product quality. P.L.480 research totals 12.5 man-years, of which 7.7 is on effect of fiber properties on processing efficiency and product quality and 4.8 is on development of new and improved methods and instruments for measuring physical properties of cotton.

The following lines of work were terminated during the year: (1) Development of an accelerated spinning ends down test for rapidly evaluating the processing efficiency of cotton; and (2) Development of apparatus and methods for automatically preparing cotton fiber specimens suitable for scanning and rapidly obtaining accurate fiber-length and length-distribution measurements (under development of new and improved methods and instruments for measuring the physical and chemical properties of cotton).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 0.5 professional man-years effort in this area, all under the subheading effect of fiber properties on processing efficiency and product quality. Basic research, cooperative with USDA is being conducted to relate the laboratory performance of cotton fabrics, with or without special treatments, to the inherent properties of raw cotton fibers. Fiber properties such as strength, elongation and crystallinity are of special interest in relation to fabric behavior under tests to discover such qualities as crease recovery and resistance to tearing and abrasion.

Industry and other organizations -- including cotton textile manufacturers, textile schools, and industry-supported research institutions--are conducting limited amounts of processing research to develop information to guide them in the selection of cottons for their products and obtain optimum use of available domestic Upland cottons. Their estimated annual expenditures in the United States on research on the interrelations among fiber, yarn, and fabric properties of cotton are equivalent to approximately 10 professional man-years. The investigations are generally aimed at determining the effect of the important fiber properties on spinning performance and product quality, and determining the effect of processing variables on product quality and processing efficiency, particularly on spinning and weaving performance. Close cooperation between industry and the Southern Utilization Research and Development Division makes research information readily available to industry. For example, considerable Southern Division effort has gone, and is going, into research to evaluate the effect of length distribution in cottons on product quality and spinning performance. Many papers have been published by the Division on this subject in industry journals having wide circulation,

and others have been presented at widely attended industry meetings. Most of the findings of company research are not published and hence are not available to the entire industry.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Effect of Fiber Properties on Processing Efficiency and Product Quality

1. Effect of Cotton Fiber Properties Such as Length, Strength, Fineness and Elongation on Fabric Properties and Processing Performance. Further evaluations were made of the effect of short fibers on yarn and fabric properties and spinning performance. Short fiber (less than 3/8 inch in length) contents of 14% and above by weight have been shown to detrimentally affect yarn and fabric quality and spinning performance. The 720 spindle-hour spinning efficiency test developed during the course of the research has received considerable interest. Conventionally, a minimum of 5000 hours' testing is generally used to determine spinning performance.

Research on the effect of cotton fiber maturity (Micronaire Reading) on fabric contraction was continued and completed. Fiber maturity varies greatly by seasons and cottons and has, in the past, been an unknown factor in fabric designing to obtain a given fabric width. Crimp in warp yarns was found to increase inversely with yarn diameter, which decreased as the Micronaire Reading of the fibers increased from 2.5 to 4.0 over the twist range of 3.6 to 4.8 T.M., and then stayed the same or increased when higher Micronaire Reading (5.0 and 6.0) cottons were used, regardless of twist. Generally, the strength (grab and strip, warp and fillingwise) of fabrics was found to be significantly affected by cotton fiber fineness in both warp and filling yarns, and by twist in filling yarns. The widths of fabrics containing these yarns as filling increased with increases in fiber coarseness (over the full range investigated) and in spinning twist. After bleaching and dyeing operations, fabric widths decreased as fiber coarseness and spinning twist increased.

In experiments on heat-drying of cotton, the changes in cotton properties were found dependent both on mechanical working and on cotton dryness in all stages. The relative contributions of the two procedures in combination are difficult to establish satisfactorily. The changes during mill processing were additive and relatively independent of the gin-induced changes. The small changes in several fiber properties caused by excessive heat-drying cannot be used, singly or in combination, to identify an "over-dried" cotton; these changes are overshadowed by the variability due to varietal factors or growth conditions. Cottons from a wide range of gin practices examined showed only small differences in physical properties. Since these values are average for fibers and all portions of fibers, they cannot reveal any nonuniformity in the sample. The nonuniformity of drying may account for some heretofore unexplained reversals in trends. The research on ginning damages has been terminated and emphasis shifted to basic investigations of fiber damage in mechanical processing from opening through carding.

The small-scale, pilot-plant spinning tests on the factors affecting end breakage during spinning of cotton yarns have been completed by the contractor (Auburn Research Foundation, Inc.). For the first time these screening evaluations using an accelerated spinning test have given a relative ranking of the effect that processing variables and fiber properties have on end breakage. Even though the reliability of these screening evaluations must be confirmed

by larger scale commercial spinning tests to make the findings applicable to existing mill equipment, they nevertheless provide the industry in a gross sense with needed guidance in what variables to change (fiber property or processing) in order to reduce end breakage in spinning and utilize more efficiently fiber properties outside of the "average" quality.

New contract research has been initiated by Auburn Research Foundation, Inc. on large-scale spinning evaluations of the effect of fiber properties and spinning variables on yarn properties and end breakage during spinning. It was found in initial tests that stronger fibers offer slightly improved spinning performance over weaker fibers, with the effect being greater at lower twists. Statistical analyses of the effect of five levels of fiber strength upon spinning performance and yarn strength are now in process. (S2 1-178(C)).

Work was continued to determine the effect of the principal types of spotted cottons on product quality and processing efficiency to obtain optimum use of such cottons. The successful use of upwards of 10% of Diplodia sp. (tight-lock) and Aspergillus flavus damaged cottons in blends with undamaged white cotton indicates that cottons classed as light-spotted, or spotted, because of the presence of up to 10% of such damaged cotton in the bale, can be used by the textile industry to produce satisfactory products. Chemical finishing processes (bleaching, mercerizing, dyeing) were found to satisfactorily eliminate color differences in fabrics woven with filling yarns spun from cottons containing Diplodia or Aspergillus flavus spotted cottons (up to about 10% by weight), showing that these types of damaged cottons can be utilized efficiently in cotton textile processing. Samples of other types of spotted cottons have been obtained for evaluation of their response to mechanical and chemical processes. (S2 1-153).

A fundamental investigation of the causes of warp breakage in the weaving of cotton yarns is in progress under P.L. 480 research at the Shirley Institute. The breakage of warp yarns during the weaving of cotton fabrics is the principal deterrent to higher weaving efficiencies. Data from past weaving experiments is being evaluated through the use of a punched card system. A more detailed study is based on observations of the operations of a slow-motion model loom in conjunction with the insertion of simulated obstructions in selected warp yarns. This procedure is based on evidence which seems to indicate that breaks in warp yarns result from abrasion by obstructions and are not due to thin places in the yarns. The research is now being extended to normal, full scale weaving tests. (UR-E29-(20)-4).

In P.L. 480 research at the Juan de la Cierva School of Technical Investigations, determination is being made of the relationships between the cohesion of cotton fibers and other physical properties of fibers, rovings and yarns. The cohesion of cotton fibers affects the roll settings, roll pressures and twists to be used in producing yarns of optimum quality. The main laws governing the minimum twist of cohesion of cotton rovings and yarns in connection with testing conditions (length and tension) and fiber parameters (length and micronaire) and yarn parameters (number of fibers per cross section and twist) have been determined and an improved apparatus for measuring minimum twist of cohesion is being developed. The study is being extended to chemically modified cottons. (UR-E25-(20)-2).

2. Improved Processing Procedures to Obtain Maximum Utilization of Native and Modified Cottons. Investigations of the interactions of draft, front roll

speed, spindle speed, twist, and traveler weight on processing performance and product quality are underway to aid in the design of experiments in a new project seeking to minimize the detrimental effects of cottons with inferior length distribution characteristics (high short fiber content). Tests using the 720 spindle-hour technique and cottons with three levels of short fiber content (5, 10 and 15%) have been conducted to determine the effects of draft, traveler size, and spinning speeds on end breakage in spinning. The preliminary experiments indicate that the detrimental effects of high short fiber content may be ameliorated by resorting to lower drafts. Verification of these findings will be conducted using Arizona and California cottons harvested and ginned under carefully controlled conditions. (S2 1-179).

Research has been initiated to characterize fiber damage in mechanical processing from opening through carding to provide information needed for developing improved textile machinery and processing methods. A thorough analysis of available data was made to serve as a guide for the initial stages of the research. Re-evaluation of data from heat-drying studies and studies of various cleaning techniques shows that the increment of change in cotton properties during any one process or machine is small but the change tends to be progressively cumulative through a series of processes. The extent of change is dependent, to a considerable extent, on certain factors in the previous history of the cotton. Initial investigations of the opening and cleaning processes indicate that fiber breakage, surface damage, etc., while frequently associated are not necessarily caused by the same machine actions. This research will continue to determine the mechanism causing the damages, and the amounts and types. (S2 1-185).

The effect of drafting forces in high draft systems on cotton yarn strength and uniformity is being investigated in P.L. 480 research at the Juan de la Cierva School of Technical Investigations. Drafting forces during spinning affect the quality of cotton yarns. Of particular importance is the force generated in the drafting field by changes in speed. Limited results thus far indicate that increasing the drafting speed improves yarn strength. Means have been developed to actually measure the drafting forces in the front and rear drafting zones. (UR-E25-(20)-13).

B. Development of New and Improved Methods and Instruments for Measuring the Physical and Chemical Properties of Cotton

1. Application of New and Improved Concepts Such As Automation to the Measurement of the Properties of Cotton Important to Utilization Research Including Length, Strength, Fineness and Elongation. Contract research by the U. S. Testing Company to develop a satisfactory technique for automatic fiber specimen preparation for length-distribution measurements was completed. A rapid, new method was developed which involves clamping parallelized cotton fibers along a precisely defined base line by means of stitching the fibers to an abrasive backing material. The fiber specimen has been shown by array analysis to represent the original fiber distribution. The new technique should be adaptable to automated fiber length distribution measurement. Upon development of suitable means for scanning the present or improved specimen, and computing the length distribution, the technique should find wide practical use. In the research a theoretical approach was developed that appears to provide the basis for the development of fiber length distribution models which correct for the effect of fiber breakage. (S2 1-133(C)).

2. Development and Adaptation of Instrumental Techniques for Measuring the Changes Imparted to Cotton by Chemical and Mechanical Processes to Improve Its Properties. Neps, small tangled clumps of fibers that first become visible in the card web from the cotton carding machine, are the cause of serious irregularities or defects in cotton fabrics. The counting of neps in the card web is a necessary quality control measure in the production of fabrics, but it is difficult and time consuming. Progress is being made in P.L. 480 research at the Juan de la Cierva School of Technical Investigations toward rapid automatic scanning by an electronic device of card web samples to permit counting of neps through measurement of irregularities in the transparency of the card web. Patentability of a device developed to classify neps into size groups electronically is under consideration. (UR-E25-(20)-1).

3. Development of Methods for Evaluating the Processing Characteristics of Cotton Essential to Its Optimum Utilization. Extensive evaluation of the accelerated spinning test method developed in earlier work showed that the technique will enable a quick appraisal of the spinning performance of cottons of different qualities. The accelerated test proved to be sensitive and reproducible for evaluating the spinning efficiency of extra-long staple cotton, extending the results obtained earlier on short and medium staple lengths. Results obtained using the test correlate closely with those from the conventional 5000-spindle-hour tests for cottons of contrasting fiber properties (fineness, strength, and elongation). The accelerated test method requires only 5½ hours and a small sample to test the spinning performance of a cotton. The ability of the method to rank spinning performance of cottons due to difference in fiber properties and processing variables makes available to the textile industry a valuable tool for the rapid evaluation of "spinnability" of cottons. The research has been terminated. (S2 1-130).

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AREA NO. 3 - COTTON - NEW AND IMPROVED TEXTILE MACHINERY

Problem. Cotton is plagued by problems of trash and nonuniformity of fiber length distribution that are not present in synthetic fibers, paper, and other competitive products. Highly efficient methods of cleaning are needed by the cotton textile industry to process satisfactorily the large quantities of machine-harvested and roughly hand-harvested cottons being marketed. Last year more than ten million bales were harvested by these methods in the United States. Such cottons are difficult to clean with existing textile equipment because of the type of their trash -- largely fine, leaf trash. The development of an integrated system for opening, cleaning, and carding today's cotton can provide substantial improvements in quality and lower costs. The present cotton mill utilizes ten or more processing stages and, compared with other manufacturing systems, an excessive amount of labor. The redesign of existing equipment and the development of radically new types of processing machinery offers an opportunity for major improvements in uniformity and overall quality of textile products, and for savings in manufacturing costs through decreased waste of spinnable fiber, and through reductions in machinery investment, space, and labor.

USDA PROGRAM

The Department has a continuing long-term program involving mechanical engineers, physicists, and cotton technologists engaged in research to design and develop new and improved equipment for processing cotton into higher quality, lower cost consumer products. Research to develop improved mechanical processing machinery, for opening through carding, is conducted at New Orleans, Louisiana. This work includes the development of experimental machines and pilot scale machines for evaluation under pilot-plant conditions, and subsequent development of plans for scaling up successful units into practical, commercial size equipment. Current research involves the development of a bale-breaker-blender for opening and blending cotton, the improvement of cleaning at the card, and the development of a machine for removing short fibers from cotton. Close cooperation is maintained with cotton textile machinery manufacturers and cotton textile processors in the establishment and dissemination of engineering specifications for the commercialization of new and modified processing equipment. The Cotton Division, AMS, is cooperating under a memorandum of understanding in evaluating the SRRL Non-Lint Tester, a recently developed machine for determining trash content of lint cotton.

The Federal scientific effort devoted to research in this area totals 11.1 professional man-years. All of the present effort is on the development of improved mechanical processing machinery-opening through carding.

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported no work in this area.

Industry and other organizations---including textile machinery manufacturers, textile mills, and private research organizations---expend an estimated 340 man-years of effort annually on research to develop new and improved textile processing machinery of which only 30 man-years are on research to develop

machinery to improve and extend the utilization of cotton. The research program of the cotton textile industry is largely limited to research conducted by textile machinery manufacturers with the objective of improving their conventional type processing equipment and of developing new equipment of conventional character. Practically no fundamental research is carried out, but rather the work is concerned with modifications of basic processing machines that originated up to 200 years ago. For the past decade textile equipment manufacturers have concentrated on the development of spinning machines that will efficiently process cotton, synthetics, and cotton-synthetic blends; higher production drawing frames; and improved looms for weaving standard construction fabrics.

Machinery manufacturers, private research organizations and textile mills maintain close contact and freely exchange technical information in the area of equipment development with the Southern Utilization Research and Development Division. Industry has rapidly commercialized the results of the Southern Division's machinery research, as evidenced by the fact that 76 patent licenses have been granted to produce the Division's widely used SRRL series of cotton textile machines.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Improved Mechanical Processing Machinery - Opening Through Carding

1. Equipment for Blending Cottons of Different Fiber Properties to Produce Improved Cotton Textiles. Cotton varies widely in fiber properties within and between bales, and there is a vital need in the industry to blend bales into a homogeneous mass to avoid production of inferior quality textiles. Research has been continued to design, construct, and evaluate a pilot model bale-breaker-blender, thereby providing the industry with an urgently needed method for improved blending.

An experimental bale-breaker-blender was modified and tested. The test results demonstrated that the fundamental motions of the modified machine were basically sound. The use of hooked pins in lieu of straight pins on the processing cylinders has proven very satisfactory. A new feed system was installed and has eliminated many difficulties encountered in feeding and doffing. Final evaluation has been made of the experimental model machine. An adequate production rate has been achieved with it, equivalent to 500 lbs./hr. in a full size machine. All design phases and working drawings of a half-size prototype machine have been completed, and construction started. (S2 1-154).

2. Equipment for the More Efficient Removal of Foreign Matter from Cotton. Research studies on combining controlled airflow with selected grid bars, baffles, and contoured screens have led to further improvements in the machine for rapidly determining the "non-lint" or trash content of lint cotton. The final model machine, called the SRRL Non-Lint Tester, is a completely self-contained and compact unit capable of 90 to 95% cleaning efficiency at 30 pounds per hour production. Trash content of a bale of cotton can be determined in about 3 minutes with the new machine, as compared with one hour for the conventional machine. The Non-Lint Tester is being evaluated by the Cotton Division, AMS, on a wide range of American Upland cottons; results to date have substantiated SRRL findings. The Tester will help manufacturers produce higher quality cotton products by

aiding in selecting cottons of optimum cleanliness for specific end products and in adjusting cleaning equipment for maximum efficiency. It will also be of value in research to develop more efficient cotton gin and textile mill cleaning equipment.

3. Improved Cotton Carding Machinery for Better Cleaning Fiber Separation and Orientation. Practical methods and modifications for improving the cleaning efficiency of the cotton textile card have been sought. The aerodynamic function of mote knives below the lickering of the card has been investigated and found to play an important part in determining the amount of lint separated at that point. Simple changes in mote box arrangements have reduced turbulent air to a controlled flow and have thus improved cleaning, reducing the trash content of card sliver as much as 35%. Informal testing in a commercial mill of the mote box modification (now designated "Fiber Retriever") showed that the trash removed in the motes was doubled while the lint loss was reduced 25%.

The principle of the "Fiber Retriever" makes it practical from the standpoint of low lint loss to use multiple cleaning stages at the lickering section of the cotton card. It has been determined that the conventional sharp-edge, closely-set type of cleaning bar is not as effective in removing fibrous trash as a properly designed blunt edge at a wide setting. In other work, a relatively simple and compact mechanism has been developed for multiple stage cleaning. Two cleaning stages (employing blunt edge cleaning bars) on a 9" diameter lickering are producing better cleaning than three stages. A feed system is being investigated which uses the prepener roll of the granular card as a feed roll thereby making more of the lickering periphery available for cleaning. An investigation will be made of the relationship between number of cleaning stages and lickering diameter as affects cleaning rate. (S2 1-137).

4. Machine for Removing Short Fibers from Cotton. The presence of excessive quantities of short fibers (3/8" and shorter) in cotton has an adverse effect on mill processing efficiency and product quality. Preparatory to initiating developmental work on a machine for removing short fibers, a literature search was made to study previous work relative to removing short fibers and to investigate basic principles having possible merit as research approaches to the problem.

A prerequisite to any method for separating short fibers from lint cotton is an efficient means for obtaining well-opened individualized fibers. In initial development work, feeding and opening means for supplying individual fibers into an air stream were designed and constructed. One arrangement places the fibers in a low velocity air stream, the other a high velocity air stream. At the present stage of development, the former appears more promising.

A fundamental study of the reaction of the individualized cotton fibers in electrostatic fields has been made. It was found that fiber alignment and fiber fractionation can be obtained through the application of an electrostatic field. Although all previously reported research reported that cotton fibers of all lengths react identically under the influence of electrical forces, present investigations have shown indications of fiber length differentiation in an electrostatic field.

It is planned to continue research on electrostatic fiber length group fractionation. Concurrent with this work, mechanical means for accomplishing short fiber removal will be studied. Construction is underway on a device based on the principle of continuously brushing a strand or web of cotton fibers through a system of brushes. (S2 1-164).

B. Improved Mechanical Processing Machinery - Drawing through Weaving

1. New Methods and Machines for Spinning Improved Cotton Yarns. Modifications of the SRRL Ringless Spinning Machine for spinning cotton yarns without the conventional ring and traveler system have resulted in improved performance, enabling the spinning of high twist medium coarse yarns at a production rate equal to that of many standard spinning frames. The machine winds the yarn directly from the spinning spindle into packages of any shape or size needed for later processing steps, thus eliminating the time and labor required in conventional ring spinning to change bobbins and rewind the yarn. The experimental work is now complete, and the research results have been released to the textile industry. One of the largest manufacturers of textile machinery in the United States is currently making a mechanical and economic evaluation of the experimental model.

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Improved Mechanical Processing Machinery - Drawing Through Weaving

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AREA NO. 4 - COTTON - IMPROVEMENT OF WASH-WEAR PROPERTIES

Problem. Garments which are wrinkle resistant and suitable for wash-wear use are increasingly important to the consumer. Although much progress has been made toward securing this market for cotton, much additional information is needed to hold and expand cotton's share of this enormous market. According to current industry estimates 1.2 million bales of cotton are used annually which would not have been utilized except for the wash-wear development. Projected estimates indicate that in the future most apparel and almost all household textiles will be given a wash-wear or a minimum-care finish. Research on synthetic fabrics is mainly aimed at this lucrative market and is five times greater than the entire utilization effort on cotton. At the same time chemical firms are reducing their research in the development of cotton wash-wear finishes. Promotional advertising claims on cotton wash-wear products have exceeded the actual achievement, and many problems remain to be solved. Much fundamental information is needed to explain mechanisms of the reaction of cotton with crosslinking agents as a basis for the development of new and better wash-wear finishes and for the improvement of present processing techniques. Much applied information is needed which, while essential to the maximum utilization of cotton, is generally beneficial to all processors and therefore comparatively unattractive financially to individual companies. Areas in which research is needed to improve wash-wear cottons include processing techniques, fabric appearance, durability, and comfort. Fabric appearance involves the ability to dry smoothly, resistance to wrinkling or mussing during wear, resistance to dry, wet, and oil soiling, introduction of durable creases as desired, dimensional stability and elimination of seam pucker. Durability involves tensile and tearing strength and abrasion resistance in the finished fabric as well as resistance to abusive laundering, particularly bleaching and souring. Comfort involves moisture absorption during use, elimination of odor on storage or wearing and, in certain cases, stretchability of fabric.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists, physical chemists, analytical chemists, physicists, microscopists, chemical engineers, mathematicians, cotton technologists, textile technologists and textile engineers engaged in both basic and applied research on wash-wear finishing and improvement of wash-wear properties of cotton. Informal cooperation is maintained with textile finishers, chemical manufacturers, and textile research institutes in connection with the research. Basic and exploratory research on wash-wear finishing of cotton is conducted at New Orleans, Louisiana. This research is designed to give a better understanding of the chemical reactions and physical changes taking place in wash-wear finishing and the crosslinking of cotton in general. It also seeks to correlate the properties of the finished cotton with the chemical structure of the crosslinking agents. The results provide a broad and sound foundation for the development of new, practical wash-wear finishes for cotton. Additional basic and exploratory research is carried out under contract at Lowell Technological Institute Research Foundation, Lowell, Massachusetts, on reactive finishing agents for wash-wear cottons. Research on the improvement of smooth drying properties--the essential features of a wash-wear fabric--is conducted at New Orleans, Louisiana. Important phases of current work involve studies of the controlled reaction of formaldehyde with cotton to produce smooth drying fabrics having improved abrasion and

tear resistance; development of new crosslinking treatments and optimum wash-wear fabric structures; combination of chemical and mechanical treatments to improve strength and resilience; and pilot-plant evaluation of promising laboratory finishes. Additional research on improved smooth drying properties is in progress under contract at the Fabric Research Laboratories, Dedham, Massachusetts, on investigation of the relationships between fabric structure and ease-of-care performance; and at North Carolina State College, Raleigh, North Carolina, on the effects of mechanical treatments of fabrics prior to, during and following resin finishing on ease-of-care properties. Research to develop new and improved processing methods for the treatment of cotton yard goods and garments to impart wash-wear properties is carried out at New Orleans, Louisiana. An important objective of one of these studies is to develop wash-wear cotton fabrics and garments with durable creases and shape holding properties. Processing methods are being investigated for the production of wash-wear fabrics with greater and more durable stretch, a property currently highly desired by consumers. Methods of crosslinking stretch cotton to stabilize the fabric and make the increased stretch durable to laundering are undergoing study. Other phases of processing research have included studies of methods of drying and curing in the resin finishing of cotton. Cost estimates for new chemicals and for processing of cotton are made to aid industrial establishment of the research developments.

The Federal in-house scientific effort devoted to research in this area totals 30.3 professional man-years. Of this number 11.9 is devoted to basic and exploratory research on wash-wear, 12.3 to research on improved smooth drying properties, and 6.1 to new and improved processing methods. The contract research involves an additional 2.3 man-years, 0.6 being on basic and exploratory research and 1.7 on improved smooth drying properties.

The following lines of work were terminated during the year: (1) Basic research on the role of catalysts in the mechanism of the reactions of wash-wear resins with cotton; and (2) Evaluation of the physical properties of cotton chemically or physically treated to enhance their wash-and-wear values (under basic and exploratory research on wash-wear).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 2.0 professional man-years effort in this area, all under the subheading improved smooth drying properties. Crosslinking of cotton to produce a wash-and-wear type fabric is receiving research attention at one location. Objectives are to improve or develop new wash-and-wear cotton fabrics of improved wrinkle resistance.

Industry and other organizations conduct a sizable amount of research in this area. Approximately 40 organizations -- manufacturers of finishing agents, textile finishers, and textile research institutes -- are carrying on research to improve wash-wear cottons. Total estimated expenditures amount to approximately 51 professional man-years per year. The fundamental research is estimated at 6 professional man-years. Greater emphasis is on obtaining improved smooth drying properties with the objective of obtaining a superior product at equal or less cost. Research now being done, mainly by chemical manufacturers, includes new finishing agents, improved methods of testing or evaluation, and some work on improved fabric construction,

and is estimated at 28 professional man-years. Another major field of effort, particularly by textile finishers, is on new and improved processing methods, on which it is estimated that an average of 17 professional man-years of effort are expended.

Industry depends heavily on Federal research of a fundamental nature and cannot cover the field of applied research completely. There is inadequate research being done in industry on necessary work which will benefit the whole industry. In general, industry does not expend large sums on research that will benefit other companies equally as well. On the other hand, this is the type of Federal work which will bring the largest monetary returns to the industry, and will do the most to increase utilization of cottons. In the fields of both fundamental and applied research there is wholehearted cooperation between industry and scientists at the Southern Division.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Basic and Exploratory Research on Wash-Wear

1. Mechanisms of Crease Resistance and Crease Recovery. Fundamental research has been conducted to obtain information on the role of catalysts in the mechanism of the reactions of wash-wear resins with cotton to facilitate selection of suitable catalysts and optimum conditions for producing improved wash-wear cotton textiles. A study of the effect of acidic catalysts (zinc nitrate, zinc chloride, magnesium chloride and magnesium nitrate) in the cellulose-dimethylolethylene urea (DMEU) reaction showed that the rate of reaction varied with the catalyst, and that the catalyst entered into the reaction by forming a coordination complex with the DMEU molecule through formation of nitrogen-to-metal ion bonds. The reaction was studied at 45°, 55° and 65°C. with each catalyst, and found to be pseudo first order when followed to two-thirds completion. The catalyst, when ranked according to greatest to least effect upon reaction rates, followed the order: $\text{Zn}(\text{NO}_3)_2 > \text{ZnCl}_2 > \text{MgCl}_2 = \text{Mg}(\text{NO}_3)_2$.

Evidence obtained from infrared absorption spectra on the finished fabrics indicated that DMEU reacted with cotton preferentially at the primary alcohol groups. The concentration of a given catalyst used was found to influence the final properties of the treated fabric. Correlation of chlorine-scorch damage data indicated that damage during chlorine-scorch tests on the treated fabrics was due to a free radical mechanism in which the metallic complex was an important factor. Additional support of the free radical mechanism was obtained with photochemical reactions of chlorinated finished fabrics in the presence of free radical initiators. The project has been terminated. (S2 1-150).

Basic understandings of mechanisms in wrinkle formation and recovery are necessary to select optimum conditions and limits of chemical and physical treatments needed to produce superior wash-wear cotton products. To obtain information of this type, fabrics and yarns were treated with tris-1-aziridinyl phosphine oxide (APO), dimethylolethylene urea (DMEU), dimethylol urea (DMU), methylated melamine formaldehyde (MMF), and formaldehyde -- some common modifications used in the production of wash-wear fabrics. Strains were applied during selected treatments and curings. The formaldehyde treatment was used to secure wet and dry wrinkle recovery. Catalyst effects were studied with the DMU-treated fabrics. The treated fabrics were evaluated

for wrinkle recovery and fabrics, yarns and fibers were tested for tensile recovery.

The investigations to determine relationships between fabric wrinkle recovery and tensile recovery properties at various strains indicated that elastic recovery is the most important factor in wrinkle recovery but fiber properties such as modulus and friction, and fabric construction are important factors in these relationships. Tensile recovery properties differentiated between acid and alkaline catalyst in DMU treatments, but catalyst effects could not be detected in wrinkle recovery measurements. Recovery time is an important factor in these relationships. If fabric construction is constant, a decrease in thickness increased the wrinkle recovery and improved the wash-wear rating. Such a relationship has potential as a rapid and continuous method in production control.

Time effects on wrinkle recovery are greater in the case of formaldehyde treated fabrics than for the other treatments studied. The tension effects are less. A probable explanation is the lower swelling achieved under tension thus reducing the gains from application of tension.

Tension applied to fabrics in warp and filling direction increased strip breaking strength, decreased elongation and increased modulus. Tearing strength, toughness and wrinkle recovery angle changes were small. Pre-mercerization caused a large increase in wrinkle recovery angle. Tension effects on wrinkle behavior and tensile properties were essentially identical for APO, DMEU, and MMF treatments. The effects of tension on strength changes for very dry yarns are similar to those of resin treatment indicating that hydrogen bonding in the absence of moisture is comparable to crosslinking of primary valence bonds. Pilot plant evaluation of tension effects will be conducted under contract. (S2 1-155).

Research has been initiated to determine the effect on wet and dry crease recovery caused by crosslinks in different regions or between different structural elements of the cotton fiber. Different types of crosslinking agents, and a variety of crosslink distributions with different degrees of swelling, will be investigated. The data developed to date are insufficient for an analysis of the crease recovery mechanisms involved. (S2 1-189).

2. Variations in Physical Properties of Cotton Induced by Crosslinks of Different Chemical Structure. Contract research at the Lowell Technological Institute Research Foundation has been directed toward the development of reactive finishing agents for cotton that might provide improved elastic and strength properties by the introduction of cellulose crosslinks of optimum size and structure. Bis(methanesulfonates) of ethylene glycol and a number of polyethylene glycols have been successfully prepared. These compounds, which form a series of crosslinkers of varying chain length, were applied to cotton. The structure and length of the crosslink was found to have little or no influence on the relation of strength and crease recovery.

Another particularly significant result of the research was the development of a method for maintaining fiber swelling in dry-cure treatments of cotton by the use of additives. It has been found that the application of water-soluble, nonvolatile, nonreactive organic compounds with DMEU resin preserves the water-swollen structure of the cotton fiber during high temperature curing.

The use of additive compounds in this manner can broaden the technique of textile finishing and offer new insight into the role of submicroscopic fiber structure in the mechanism of crosslinking (S2 1-148(C)).

If maximum quantities of cotton fabrics are to be used in wash-wear goods, crosslinking treatments must be developed that will produce a high degree of smooth drying properties and have both hypochlorite resistance and acid resistance, without causing excessive strength loss of the fabric or raising costs beyond acceptable limits. N-Methylol finishes for wash-wear cotton fabrics are being developed which are equivalent in most respects to the non-nitrogenous finishes. Thus, the advantages of relatively low cost, convenience, high efficiency, and minimum fabric damage of the N-methylol agents are being utilized without the usual disadvantages.

Initial studies on selected dimethylol amides showed that they produced finishes with increasing acid resistance in the order: DMEU, uron, urea, carboxylic acid amide, carbamate. Dimethylol monocarbamates gave improved wash-wear finishes, and were selected for further investigation.

Finishes produced from dimethylol ethyl carbamate (DMEC) proved to be particularly promising. They are durable to multiple launderings, resistant to chlorine damage, and the treated fabrics have a high degree of wet and dry wrinkle recovery. Scale-up, storage, hydrolysis in commercial laundering, and related problems appear to be minor; and the cost of these finishes should be low. Preliminary investigations also indicated that the finish produced by tris(N-methylolcarbamoyl)ethylamine (TMCEA) is not susceptible to the usual drawbacks of N-methylol agents and can be applied efficiently without unusual loss of strength. Fabrics produced by finishing with N-methylol derivatives of ethylenediformamide have been found to be very acid resistant. However, damage from chlorine appears to be a problem with these agents.

Both the DMEC and the TMCEA finishes have been taken successfully through the pilot-plant stage. The DMEC finish has achieved considerable industrial interest. Two concerns are promoting carbamate finishes through national advertising. TMCEA also has strong industrial possibilities. One industrial firm has already expressed interest in this finish. Continued evaluations of storage, dyeing, and other factors pertaining to these two finishes are needed. Finishes based on methylolated N, N, N', N'-tetrakis (2 carbamoyl)ethylenediamine will be studied. (S2 1-177).

B. Improved Smooth-Drying Properties

1. Controlled Reaction of Formaldehyde With Cotton. Research was continued on crosslinking of cotton in the partially swollen state with formaldehyde and other aldehydes to impart wrinkle resistance to the fabric without excessive strength loss.

Laboratory experiments showed that calcium chloride can be substituted for acetic acid in the Form-D (dry and wet wrinkle resistance) formaldehyde process. This is potentially a much less expensive process. Application of certain softeners prior to treatment with formaldehyde reduces the reaction time and in some instances improves the strength.

Cotton fabrics pretreated with polyethylene and then treated by the Form-D process had higher wrinkle recovery and combined formaldehyde in a given reaction time than when no pretreatment was employed. Dry wrinkle recovery can also be increased considerably in the Form-W (wet-wrinkle resistance) formaldehyde process by pretreatment with polyethylene.

Of several aldehydes investigated, formaldehyde appears unique in imparting satisfactory wet and dry wrinkle resistance to cotton. Based on these findings, a thorough and systematic investigation of the controlled reaction of formaldehyde with cotton cellulose was undertaken as a basis for developing superior, highly durable wash-wear finishes for cotton.

A simple process has been found that will impart dry wrinkle resistance to Form W (wet wrinkle resistance) formaldehyde fabric. Fabric is first given the Form-W finish, then it is impregnated with a latent acid catalyst and cured for a short time at 140-160°C. This produces a fabric which has smooth-drying properties on drip or tumble drying. Furthermore, the product has high moisture regain, an important comfort factor.

Formaldehyde is an especially attractive reagent for producing a durable wash-wear finish, yet it has one real weakness - it causes excessive strength loss in cotton. Some conditions have been identified which minimize the loss in strength in treated cotton. The cotton must be in a slightly swelled condition to maintain greatest strength and have wet and dry wrinkle recovery. Acid degradation of the cotton in a wet formaldehyde treatment has been found to be less than in a dry-cure treatment. Acid and alkaline stability of the finish in the case of the wet treatment is relatively high but less than that of a dry-cure treatment. Mercerization before treatment improves the final strength only if done under tension.

The research has given clues to the fundamental relation between cellulose structure, crosslinking, and crease recovery. These clues are provided by the varying crease recovery-formaldehyde ratios in cotton treated with formaldehyde under different conditions and by the different response in viscose and cotton to variations in treatment.

A rapid loss of formaldehyde from fabric between drying and curing steps has been observed, which is possibly an important cause of the inconsistencies often observed in dry formaldehyde treatments. This has been circumvented by combining drying and curing into a single step. No significant loss in formaldehyde content and very little loss in wrinkle recovery was observed in cotton fabric treated by the Form-D process (calcium chloride method) after repeated home laundering.

It has been discovered that magnesium chloride-citric acid mixture is an efficient catalyst, promoting rapid reaction in crosslinking of cotton cellulose with formaldehyde. Starch-polyethylene has been found to be a good strength builder when producing wash-wear cotton fabrics by reaction with formaldehyde. Emphasis in further research will be on improving the strength of the formaldehyde-treated fabrics. (S2 1-166).

2. Development of New Crosslinking Treatments to Improve Strength and Resilience of Cotton. Crosslinkage is a powerful tool for improving the ability of cotton fabrics to resist wrinkling during service. Improvements in smooth drying, wrinkle resistant, strength and other desirable

properties are being sought by application of crosslinking agents to various chemically modified cottons. Hydroxyethylated, carboxymethylated, acetylated, and cyanoethylated cottons have been investigated.

The reactivity of cotton cellulose with formaldehyde crosslinking agent was increased threefold by introducing a low degree of hydroxyethyl groups. The presence of the hydroxyethyl groups does not prevent the development of dry wrinkle resistance. The crosslinked hydroxyethylated cotton has much higher moisture regain than crosslinked cotton. Reaction of carboxymethylated cotton with formaldehyde, even in low water content media, did not produce dry wrinkle resistance.

Fabrics with good wet and dry wrinkle resistance, approximately 90% retention of original breaking strength, higher moisture regain than native cotton, and good resistance to loss of strength in the chlorination-scorch test were obtained by treatment of the free carboxyl form of carboxymethylated cotton with triazine or ethyleneurea crosslinking agents without added catalysts.

The importance of crosslinking chemically modified cottons in certain regions is illustrated in the results obtained upon treatment of partially hydrolyzed acetylated or cyanoethylated cotton. The research has indicated that the substituent groups removed by hydrolysis makes different hydroxyl groups available for the crosslinking reaction than those which are available after esterification or etherification to the corresponding degree of substitution.

It has been found that urea-formaldehyde or DMEU-treated carboxymethylated cotton fabrics are markedly more resistant to damage in the rigorous scorch test than the corresponding treated unmodified cottons even though the fabrics are chlorine retentive. This resistance may be due to a neutralizing effect of the carboxyl groups which are present as the sodium salt after treatment of the fabric with sodium hypochlorite. This fundamental information could be of practical value to the cotton finishing industry and to research directed to the development of cheap, chlorine-resistant, wash-wear cottons. Additional study will be carried out on chlorine-retentive, damage-resistant fabrics prepared by treatment of other carboxyl-containing chemically modified cottons. (S2 1-171).

3. Development of Optimum Wash-Wear Fabric Structures. Procedures are being sought to modify standard cotton fabrics employed in wash-wear and easy to care for garments by making appropriate changes in yarn and fabric structures so as to give the fabrics optimum wash-wear performance and maximum utility when resin treated.

Cottons selected for fiber properties differing in strength, elongation and fineness have been spun into filling yarns, and woven as filling using a standard printcloth warp. The fabrics were treated with DMEU resin and evaluated for wash-wear rating. Initial results indicate that fabrics woven with 40/1 filling yarns have better smooth-drying properties than fabrics with 45/1 or 35/1 filling yarns; and there is no apparent correlation between wash-wear rating and filling twist multiplier. The tensile strength of the resin-treated fabrics was directly proportional to the original strength of the fibers from which they were made. For the fabrics constructed from the high-strength fiber, with twist multipliers (T.M.) higher than 3.0, the finest yarn made the fabric of highest tensile strengths. At 3.0 T.M., however, the coarsest yarn fabric was strongest. For the low strength fiber, the coarsest

yarns made the strongest fabric at all T.M.'s. Tear strength, in general, was highest for fabrics made from the coarsest yarn and increased with increasing T.M. Abrasion resistance improved considerably as T.M. increased and yarn size decreased.

Preliminary experiments to determine the effect of type twist on the wash-wear properties of DMEU-treated fabrics have been completed. The print cloth test fabrics were made from a common warp of Z-twist yarn, using filling yarns of several different twist multipliers in both S- and Z-twist woven singly and in combination. No significant differences were observed in the effect on wash-wear rating of either twist-type combination or yarn twist multiplier. Because of the possible interaction between the warp and filling yarns in a fabric, it may be desirable to repeat the experiments with both warp and filling varying in twist types and combinations thereof. (S2 1-163).

Research has been initiated under contract at Fabric Research Laboratories to investigate the relationships between ease-of-care performance and the geometry (structure) of cotton fabrics. The causes for wrinkles will be studied, and characteristics of fabrics which wrinkle and do not wrinkle under a range of moisture and temperature conditions will be established. Initial experimental work has involved studies of twenty-one fabrics of four general types (print cloth, broadcloth, sateen and twill), treated as mercerized and bleached, with DMEU and APO at levels of 4% and 7%, respectively. Within fabric types, structure effects on wrinkle recovery were slight at standard atmospheric conditions. Mercerization caused beneficial effects on tearing strength. The APO resin on mercerized fabric produced the most desirable finish. Future research will be directed toward the determination of wrinkle recovery and fabric rigidity under ranges of temperatures and moisture conditions. (S2 1-170(C)).

C. New and Improved Processing Methods

1. Development of Durably Creased, Shape-Holding Garments. Excellent progress has been made in research to develop wash-wear cotton fabrics and garments with durable creases and shape-holding properties. The production of durable creases and pleats in wash-wear cottons is difficult or impossible by conventional means since the finish is designed to prevent permanent deformations.

Cotton fabrics and garments have been treated to produce durable creases, smooth drying properties, and dry wrinkle resistance by pressing the fabric or garment to place creases where desired and then immersing the fabric or garment in a formaldehyde-catalyst solution of relatively low swelling capacity which crosslinks the cotton in the desired configuration. It has also been found that creases can be produced in cotton fabric by pressing the creases where desired and then striping a formaldehyde-catalyst solution of low swelling capacity along the crease which crosslinks the crease in place.

A simple procedure was developed for introducing durable creases into wrinkle resistant cotton fabric. The process involves striping the area to be creased with formic acid or lactic acid solution and ironing-in the desired crease. This could be an attractive technique for garment cutters to produce cotton trousers and jackets with the shape holding characteristics demanded by current fashions.

Numerous crosslinking agents and catalysts have been successfully applied in a deferred cure process for producing durable creases and wash-wear properties in cotton. In the process, yardgoods are impregnated with the treating agent, but the reaction (or cure) of the agent with cotton is delayed until the garment is sewn and shaped. Carbamate crosslinkers have been found to be particularly outstanding in this process. A procedure to determine the amount of formaldehyde evolved from fabric treated with N-methylol finishing agents by the deferred cure process was devised in the course of the research.

A process was developed for the treatment of cotton sewing thread to eliminate or greatly decrease seam pucker. The thread is impregnated with crosslinking agent and catalyst, dried at low temperature such that crosslinkage does not take place, sewn into the seams of a garment, and heat cured after sewing.

Studies of various techniques for the application of fluorescent whitening agents in wash-wear finishing of cotton have shown that application of the proper combination of whitening agent and crosslinking agent from the same pad bath with curing in the conventional manner produces excellent whiteness and wrinkle resistance, which effects are durable to various laundering procedures.

A high tension during the curing step of conventional wash-wear finishing has been found to result in poorer wash-wear properties, i.e., "permanent rumple", after laundering if the finish has poor durability. It has been shown that stretching a fabric during crosslinking does not affect the smooth drying properties of the fabric if the crosslinks are durable. These results emphasize the desirability of using durable type crosslinking agents in commercial processing of wash-wear cottons.

A textile structure with good wash-wear properties, strength, and abrasion resistance was prepared by bonding untreated cotton to urethane foam or to wash-wear cotton fabric. It is particularly useful for collars and cuffs. This research development has evoked considerable industrial interest. One large finishing company is conducting a thorough investigation of the process and has already finished several thousand yards of collar material for evaluation.

Wash-wear cotton fabrics with greater and more durable stretch are currently highly desired by consumers. In a recently initiated phase of work, stabilized all-cotton stretch fabrics have been produced by crosslinking slack mercerized cotton fabrics. The products are resilient, have low permanent set, are resistant to growth, and these desirable effects are durable to repeated laundering. The crosslinking of the fabrics has little effect on elongation at a given load, although breaking strength and consequently ultimate elongation are somewhat reduced. The percentage of recoverable stretch is significantly increased by the crosslinking. Wet crosslinking of cotton stretch fabric by the Form W or Form D formaldehyde treatments causes greater loss of strength than crosslinking with DMEU resin by conventional pad-dry-cure finishing. These studies are continuing. (S2 1-162).

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AREA NO. 5 - COTTON PRODUCTS WITH SPECIAL PROPERTIES

Problem. In many uses where special properties are of paramount importance, cotton is being replaced by synthetic materials. To improve its position in the textile market, which has declined from 79.5% of mill consumption of all textile apparel fibers in 1939 to an estimated 61% in 1961, new applications must be explored and improved products developed to meet the competition of synthetic fibers. Cottons having high recoverable stretch, durable loft, light-weight bulk, pleasing textures, warmth and other highly desirable properties are needed to enable cotton to compete successfully with synthetic fibers in the rapidly expanding market for stretch and bulked type fabrics. Fabrics designed to achieve increased resistance to tearing and abrasion, flex life and other strength properties are needed to improve the wear life of cotton textiles for apparel, household and industrial uses. Cotton fabrics must be designed to withstand better the elements of weather and finishes developed that will provide greater protection from solar radiation, microorganisms, acids and fire, and that will resist color change. Cotton fabrics with improved heat and scorch resistance are needed in the commercial laundry industry and for home ironing board covers. Additional basic information must be developed to improve cotton's resistance to water and oil-borne soils, and to dry soiling. Resistance to soiling ranks fifth in importance among the 40 end-use qualities for textiles. Cheaper and durable flame retardant finishes for cotton, specially for outdoor use, are needed. Numerous consumer preference surveys have shown that a great potential demand exists for cotton material that will be more lustrous without sacrifice of functional properties. Cotton textiles with multi-purpose finishes are also needed, particularly those where several desirable end-use properties can be introduced in a single process.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists, analytical chemists, physical chemists, physicists, microscopists, chemical engineers, cotton technologists, textile technologists and textile engineers engaged in both basic and applied research to develop new or improved cotton products possessing special properties to meet the competition of synthetic fibers and other synthetic materials in various end uses. Informal cooperation is maintained with textile finishers, chemical manufacturers, and textile research institutes in connection with the research. Research is carried out at New Orleans, Louisiana, in cooperation with the Foundation for Cotton Research and Education (affiliated with the National Cotton Council of America) and the Canvas Products Association International, to develop cotton fabrics with improved resistance to outdoor weathering. This research includes discovery of new and more effective fungicides, and sunlight and microbial resistant pigments for cotton textiles; and development of improved formulations, equipment and procedures for producing weather resistant cotton textiles. The heat and scorch resistant properties of partially acetylated cotton have been evaluated on a cost-performance basis in a comprehensive field test for laundry textiles and on a smaller scale in plastic laminates, in research at New Orleans, Louisiana. Research to develop new fluorochemical finishes for oil- and water-repellency and other reactive and additive finishes is conducted at New Orleans, Louisiana, to improve cotton's soil resistance. Additional research is being performed under

contract at the Harris Research Laboratories, Inc., Washington, D. C., to provide fundamental information on the mechanism of the soiling of cotton by water- and oil-borne soils. This research includes a determination of the effects of surface change, oil and water repellency, hardness and thermoplasticity (of coated fabrics) and their relationship to the ease of soiling and soil removal from cotton. Research on flame resistant cotton textiles is performed at New Orleans, Louisiana. Emphasis has been on achieving durability of flame retardant finishes to outdoor weathering, and on the development of treatments to impart flame resistance to cotton while at the same time imparting other desired textile properties. Research to improve cotton's bulk, elasticity and resilience by resin treatment of fibers, yarns and fabrics is conducted at New Orleans, Louisiana. The research on fibers is aimed primarily at the development, by chemical or mechanical means or both, of more resilient and cohesive cotton batts for use in mattresses and other padding applications in the furniture and automobile industries. The cotton batting research is conducted cooperatively with the National Cotton Batting Institute, Textile Waste Association, National Cottonseed Products Association and the Foundation for Cotton Research and Education (affiliated with the National Cotton Council of America). Work on yarns is intended to produce bulky, elastic yarns suitable for weaving or knitting into fabrics with improved stretch and/or warmth characteristics. Investigation of a slack mercerization process, with and without subsequent resin treatment, is being carried out to achieve stretch fabrics for industrial, household and apparel uses. Additional research in the field of stretch and bulked cotton products is being carried out under contract at Lowell Technological Institute Research Foundation, Lowell, Massachusetts, on the development of bulked cotton yarns on the woolen system suitable for weaving apparel and other types of fabrics with improved warmth characteristics. Research on the effect of yarn and fabric construction on the physical properties of chemically treated cotton fabrics is another phase of work at New Orleans, Louisiana. Engineering studies are in progress to determine the feasibility and practicability of chemical and resin treatment of roving by continuous processing as an intermediate step in the mechanical processing of cotton. Chemical, resin, or combination treatment of roving could provide new and improved properties useful in such applications as heavy woven products, knitted paddings, tightly twisted or plied yarns and thermoplastic yarns. Additional research is being carried out under contract at the Philadelphia College of Textiles and Science, Philadelphia, Pennsylvania, to develop yarns by mechanical, chemical and physico-chemical methods to produce cotton crepe fabrics which will compete with those made from synthetic fibers.

The Federal in-house scientific effort devoted to research in this area totals 15.8 professional man-years. Of this total, 2.9 is devoted to weather resistant cotton fabrics, 0.5 to heat resistant cotton textiles, 4.4 to soil resistant cotton textiles, 2.4 to flame resistant cotton textiles, 3.3 to stretch and bulked cotton products and 2.3 to effect of yarn and fabric construction on the physical properties of chemically treated cotton fabrics. The contract research involves an additional 1.9 man-years, 0.9 being on soil resistant cotton textiles, 0.5 on stretch and bulked cotton products, and 0.5 on the effect of yarn and fabric construction on the physical properties of chemically treated cotton fabrics.

The following lines of work were terminated during the year: (1) Cost-performance evaluation of heat and scorch resistant properties of partially acetylated cotton for laundry textiles (under heat resistant cotton textiles); (2) Research to improve the light and weathering resistance of flame-resistant cotton products (under flame resistant cotton textiles); and (3) Development of winter-weight cotton fabrics on the cotton processing system (under stretch and bulked cotton products).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 did not report any effort in this area of research.

Industry and other organizations---including chemical companies and textile mills---expend an estimated 60 professional man-years' effort on this type of research in areas in which the Southern Division is carrying out research. Of this total about 35 man-years is on chemical and 25 man-years on mechanical phases of the research. These estimates are made primarily on the basis of publications and patents, with full realization that many of the results of industrial research are never published.

Textile chemical manufacturers, while conducting some basic research, are predominantly interested in the development of textile chemicals and auxiliaries for use by and in textile mills. The number of concerns manufacturing such chemicals runs into the hundreds, many of whom have no research departments. The textile mills, in a similar fashion, are investigating new finishes and are consistently making advances in finishing technology leading to more efficient processes and superior products. Close cooperation between the cotton laboratories at the Southern Division and industry makes research information available to all segments of the industry.

Industry recognition of the value of processes developed in the Southern Division for flame resistance, rot and mildew resistance, outdoor fabrics, heat resistance, soil resistance, stretch and bulky fabrics and other properties, has led to the adoption of some of the processes, to the extent that new chemicals necessary for these treatments are now commercially available and fabrics so finished are being marketed. In many cases these have necessitated research by industry to modify existing machinery and fabric structure to suitably utilize the new finishes.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Weather Resistant Cotton Fabrics

1. Improved Fungicides, and Sunlight and Microbial Resistant Pigments for Cotton Textiles; and Improved Formulations, Equipment, and Procedures for Producing Outdoor Cotton Textiles. To make cotton fabrics better suited for outdoor use, finishes are needed that will provide greater protection from the destructive action of weathering and micro-organisms. Research was continued on the development of weather and rot resistant cotton fabrics in cooperation with the Canvas Products Association International, and the Foundation for Cotton Research and Education.

New selenium-containing inorganic compounds have been found for impregnating cotton duck to impart a high degree of resistance to mildew attack and algae

growth. These colorless and biologically effective compounds, alone and in combination with other protective materials, are being tested more extensively.

Thirty-one fungicidal compounds, primarily phenyl mercury derivatives, were evaluated as possible outdoor fungicides. In connection with the research, two new methods for solubilizing normally insoluble phenyl mercury and copper fungicides have been developed. After the solubilized metallic salts are applied to fabric and dried, they become insolubilized to impart their fungicidal properties to the cotton. Using these methods, it is possible to simultaneously apply, in a one-step method, both fungicide and water repellent. Comparative evaluation of commercial methods of applying phenyl mercurial compounds and copper-8-quinolinolate with these newly developed methods for application and solubilization indicate that at least approximately equal effectiveness is obtained and the process for application is simple.

The previously developed "formic acid colloid of methylolmelamine" weather and rot resistant treatment for outdoor cotton fabrics is now being used by a commercial firm in the production of truck covers and other similar industrial fabrics. The service performance of the fabrics has been very good, and consumers are requesting more of the products.

A thorough evaluation of the quick-cure copper formate fabric preservation process alone and in combination with selected additive materials is planned. Other areas to be investigated in the in-house research include additive and resin reactive protective treatments for outdoor cotton threads, and methods to give accelerated weathering results. (S2 1-156).

Contract research at the Texas Woman's University on modification of cotton fabrics with inorganic salts to improve weather and rot resistance and water repellency has been completed. Cobaltous metaborate and cobaltous hydroxide have been shown to provide resistance to both microorganisms and actinic degradation. The inorganic compounds can be satisfactorily applied from a suspension in commercially available latices employing a one-bath process apparently suitable for commercial applications.

B. Heat Resistant Cotton Textiles

1. Cost-Performance Evaluation of Partially Acetylated Cotton. The statistically designed schedule of service tests in a commercial laundry to establish reliable cost-performance of partially acetylated (PA) cotton laundry textiles in comparison with competitive materials has been completed. It was found that some PA cotton fabrics (1) have a performance equal to that of nylon as hot head press covers; (2) possess a favorable cost-performance advantage as flat work ironer covers; (3) make an excellent intermediate padding material for hot head presses; and (4) as blends of 70 per cent PA cotton and 30 per cent untreated cotton, perform equally well on both hot head presses and flat work ironers.

C. Soil Resistant Cotton Textiles

1. Fluorochemical and Other Soil Resistant Finishes for Cotton. The competitive position of cotton in domestic, military, and industrial applications would be greatly enhanced by the development of durable and efficient water and oil repellent finishes, and soil resistant finishes for cotton products.

The currently available water and oil repellent finishes are not durable to laundering and/or require high add-on of expensive chemicals.

The incorporation of fluorocarbon compounds with certain existing water repellent finishes for cotton is reported to produce synergistic effects on water repellency as well as produce oil repellency. Several commercially available fluorocarbons and other chemicals were incorporated in the previously developed silicone alloy water repellent finish but no particular improvement in water or oil repellency was obtained. Good crease resistance was imparted to silicone alloy-treated cotton fabric after reaction with formaldehyde and HCl in the vapor phase without affecting the water repellency.

By proper selection of the type of cellulose-reactive group, it should be possible to react cotton with fluorochemicals containing the proper number of fluorinated carbon atoms to obtain durable water and oil repellency. This approach is being explored. Since most of the currently available fluorochemicals are unsuited for direct reaction with cotton, it has been necessary to transform these compounds, by suitable synthetic methods, into materials which contain a highly fluorinated group and a cellulose-reactive group.

Certain classes of highly fluorinated compounds -- for example, derivatives of the perfluoroamides -- have been synthesized and found to be unreactive with cotton although they contain groups which are cellulose-reactive in the corresponding non-fluorinated series. Apparently the presence of the highly fluorinated radical in these compounds lowers their general reactivity. Several cyclic fluorinated halides have also been examined and found to be unreactive with alkali cotton. These same compounds, however, react with cotton treated with tris(1-aziridinyl)phosphine oxide (APO) to give durable water repellency. Long chain fatty acids applied in combination with APO impart durable water repellency to cotton. In a similar manner, perfluorooctanoic acid imparts durable oil repellency (but no water repellency) to cotton treated simultaneously with APO. The APO-based treatments offer promise for the development of good water-and-oil-repellent finishes for cotton and will be investigated further. (S2 1-180).

Soil resistance and ease of soil removal of cotton textile fabrics and fibers are important in most apparel and household cotton fabrics. There is a strong indication from findings of recent research that cotton crosslinked in a highly swelled state does not soil any more readily than cotton in a collapsed state. This is a very important factor in some of the new and better wash-wear finishes for cotton.

Fabrics crosslinked with formaldehyde in the non-swollen state (Form D) and in the swollen state (Form W), and these fabrics chemically modified to change their electrokinetic properties, are being used in the initial studies of soiling. Results indicate that the type of solid soil in aqueous and oily soiling systems plays an important part in the degree of soiling and ease of soil removal. Aqueous and oily polar red iron oxide dispersions soil cotton fabrics considerably less than aqueous and oily non-polar carbon black dispersions. Also, the red iron oxide soils are removed more readily from soiled fabrics when laundered than are the carbon black soils. Anionic groups attached to cotton improve the resistance of the fabric to aqueous red iron oxide soiling as previously found with aqueous carbon black soiling

There are indications also that certain water repellent finishes impart slightly more soil resistance to formaldehyde-crosslinked cottons than to non-crosslinked cotton fabrics. The research will continue with emphasis on cotton fabrics coated with resin films possessing varied surface properties to determine effects on soiling, and reaction of cotton with fluorine containing compounds to study effects of lowering the surface energy of fabrics with respect to soiling. (S2 1-191).

A fundamental investigation of the effects of specific type finishes on soiling of and soil removal from cotton is in progress in contract research at Harris Research Laboratories, Inc., to provide basic information to aid in designing a superior soil resistant finish for cotton. The research has already shown significant differences in soiling characteristics of cotton coated with acrylate polymers differing in hardness. The importance of temperature during the soiling process and of the polar characteristics of the fiber coating are other significant findings of initial research. Investigations of the effects of numerous finishes and chemical modifications of cotton on soiling and soil removal from cotton indicate that cationic and hydrophobic finishes soil more easily and are more difficult to clean than anionic and hydrophilic finishes. This information will be important in developing new finishes. Other surface characteristics of the cotton fiber and chemically modified cottons are to be studied so that the overall mechanism of soiling and soil removal will be better understood (S2 1-175(C)).

D. Flame Resistant Cotton Textiles

1. Weather Resistant, Flame Retardant Treatments For Cotton. Further progress was made in research to improve the light and weathering resistance of flame resistant cotton products. There is a definite need for flame retardant finishes which are cheap and withstand weathering and leaching, for use on tents, tarpaulins, boat covers, and certain types of industrial fabrics.

Flame retardant finishes based on certain esters derived from phosphonitrilic chloride have shown good durability to weathering in the New Orleans climate. The dyes present in a fabric were found to have a profound effect on the weathering durability of tetrakis(hydroxymethyl)phosphonium chloride (THPC)-methylolmelamine and APO-THPC flame retardants. Protective pigments and certain vat dyes increased the stability of the finish while light-tendering dyes greatly decreased the stability. The most effective protective pigment found was green gold. Some vat dyes, such as Flavone Yellow GC, were found to accelerate greatly the loss of resin and of flame retardancy during outdoor weathering. This shows that the resin breakdown is actually a photochemical process, and with further development may provide a new accelerated outdoor weathering method.

The outdoor service life of medium-to-heavy fabrics treated with APO-THPC flame retardant has been increased by 40-50% (to approximately 18 months by changing the mole ratio of APO/THPC used in the formulation from the standard 1:1 ratio to a 2:1 or 3:1 ratio. Vinyl coated APO-THPC treated cotton duck has satisfactorily withstood two years of weather exposure. The weathered fabric passed the standard vertical flame test, and showed an average breaking strength loss of only 15%. This compares more than favorably with the service life of the better grades of standard commercial outdoor fabrics.

In other research, it has been found that the incorporation of certain sulfur compounds, particularly sodium thiosulfate, in APO-THPC formulations improves both the resin stability and fabric strength retention during outdoor exposure. This development offers promise of extending the service life of flame resistant tentage, tarpaulins, and outdoor wearing apparel.

The research to improve the light-and-weathering-resistance of flame retardant finishes is being terminated except for tests on treated fabrics still undergoing outdoor weathering. (S2 1-138).

2. Treatments to Impart Both Flame Resistance and Improved Textile Properties to Cotton. Research was continued on the development of improved treatments to impart flame resistance to cotton, while at the same time imparting other desired textile properties. Versatile, multipurpose finishes are needed in the textile industry and could help improve cotton's position in the textile market.

Additional studies were made of the cause of the yellowing of APO-treated cotton on chlorine bleaching and scorching. Yellowing appears to be due to an oxidative effect in which the cellulose plays an important part.

A one-step process for the simultaneous application of reactive dyes and resin forming monomers, such as APO, to impart color and crease resistance to cotton has been developed. This new process is acid catalyzed and the colors produced are not removed by acid extraction. There is also a substantial increase in the depth of color of the reactive dyes over conventional application of such dyes, although the shade is slightly altered. When APO monomer is used, dimensional stability and rot resistance are imparted in addition to color, flame and crease resistance. The process has been successfully translated to pilot plant scale. APO was found superior to urea-formaldehyde type resins and diepoxides in attaching the chlorotriazine and vinyl sulfone dyes in these pilot plant runs. Wear tests are in progress on garments made from APO-dye treated fabric.

In other experiments, APO has been used to fix an embossed design as well as a dye to cotton fabric which was permanent to repeated laundering. Two new products, the formaldehyde derivatives of dibromo- and dichlorocynoacetamide, were discovered which impart flame resistance and improved crease resistance to cotton. The research to develop versatile finishes for specific end uses is continuing. (S2 1-190).

E. Stretch and Bulked Cotton Products

1. New and Improved Processes for Production of Stretchable Cotton Textiles Using Chemical Treatments. Winter weight fabrics represent a very large potential market mostly dominated by wool for many years and more recently invaded spectacularly by synthetic fiber manufacturers through use of bulk or textured yarns. Lines of work have continued to develop improved winter weight cotton fabrics (by using yarns made on the cotton processing and woolen processing systems) that will successfully compete with fabrics made from synthetic fibers and blends of synthetic fibers for outer-wear clothing and household uses.

Completed research on the production of winter weight cotton fabrics on the cotton processing system has shown that highly stretchable textured cotton

yarns can be made and woven into stretchable fabrics having improved thermal insulating qualities. The fabrics were more resilient and showed improvements in warmth properties before and after ten home launderings compared to fabrics of approximately the same weight and structure made from untreated control yarns.

The bulky stretch yarns were produced by applying a crosslinking resin (DMEU) to highly twisted plied yarns, drying and curing them in this highly twisted state and then backtwisting. Yarns capable of recovering after being stretched 200 to 300 per cent of their relaxed length were produced. The stretch-type yarns perform best in loosely woven constructions that permit the fabrics to contract. Fabrics having an elongation-at-break of over 80% were made from exceptionally loose woven double-cloth constructions containing the stretch yarns.

The demonstration that resin treated yarns can be dried and cured in package form using dielectric heating, with little or no migration of the resin, has made the process more practical and less costly. Improved resistance to wrinkling has also been obtained by retreating the stretch fabrics with resin. (S2 1-132).

In contract research at the Lowell Technological Institute Research Foundation on winter-weight cotton fabrics from yarns made on the woolen system, single and plied yarns have been produced from untreated cotton, DMEU resin-treated cotton, and blends of the untreated and treated cottons at three different levels of resin concentration and at three different twists. The yarns from the resin-treated fiber were weaker than those spun from untreated fiber. Single yarns of increased bulk have been made but they lack sufficient strength for weaving. Fabrics will be woven from selected plied yarns for evaluation. If the research is successful, the winter-weight fabrics should materially expand the market for cotton. (S2 1-140(C)).

Cotton knit goods tend to take on a "permanent set" when stretched, and hence become distorted during wear due to the limited extensibility. Contract research at Clemson Agricultural College---to develop a "Helenca-type" (elastic) yarn from cotton through the use of thermosetting resin, twist and untwist techniques, and shrinkage techniques for use in socks and other knit wear---was continued and completed. Careful screening of available types of resins normally used to produce wrinkle resistant cottons showed that DMEU produced the best stretch yarns.

Experimental yarns with good elongation and recovery which also translated into knit fabric have been produced by curing at the roving rather than at the yarn stage. Change in size and twist has yielded a much softer and more usable yarn. Improvements in elasticization or elongation have been achieved by alternately knitting paired "S" and "Z" yarns made from single yarn resin treated in the sliver form. Accurate spacing of the yarn is important if good elongation is to be obtained. Fabrics with elongations up to 200% and with 95-100% recovery have been made. The research has stimulated the interest of commercial knitting concerns in cotton stretch yarns and has provided information basic to the development of a commercially feasible stretch cotton yarn. (S2 1-143(C)).

Exploratory in-house research is in progress to produce stretchable-type

cotton yarns by setting crimp in the yarns with crosslinking resin on false twisting equipment. Based on results of preliminary experiments using a "Fluflon"-type false twist machine, the standard heating equipment has been modified to give improved stretch yarns. Treating packages of yarn with resin prior to false twisting appears to be impractical, since the yarn tends to dry out in the creel resulting in a nonuniform product. Therefore, efforts are being made to develop a suitable method of continuously applying the resin to the yarn during the false twisting operation. (S2 1-193).

2. New and Improved Processes for Production of Stretchable Cotton Textiles Using Slack Mercerization. Other research has shown that promising all-cotton stretch fabrics can be produced by a simple, inexpensive process employing slack mercerization. The effect of processing variables, yarn twist, and fabric construction are being investigated to determine optimum conditions for making stretch products by slack mercerization for various end uses, including wearing apparel, slip covers, plastic coated fabrics, boat covers and awnings.

The amount of shrinkage and consequently the quality of the stretch product is determined by the conditions of treatment and the construction of the fabric. A caustic concentration of 23% at a temperature of 25°C gives almost as much shrinkage as possible and is considered optimum for practical use. In general, greater tensions may be applied to the fabric during the caustic step than during washing and drying. Preliminary results indicate that a wide range of stretch properties can be obtained by using fabrics of different construction and weave. Fabrics woven with 20-30% fewer picks and ends produce stretch fabrics on slack mercerization that have as much as 45% elongation at the break and can be elongated 10% with very low stress. Recovery from 10% elongation or less is very good. Apparently in some cases fabric strength can be significantly increased by restretching slack mercerized cotton fabrics. Evaluation tests are in progress to determine the wearing characteristics and recovery properties of the stretch products in wearing apparel under actual service conditions.

Several companies have recently gone into commercial production of slack mercerized cotton fabrics, including those for apparel, household and industrial uses. There is considerable interest in use of cotton stretch fabrics in the manufacture of brassieres, casual wear and sportswear. Some of these end uses will be to replace stretch fabrics now made of all-synthetic or synthetic-cotton blends. (S2 1-187).

3. Resilient Cotton Batts from Low Cost Cotton. In cooperation with the National Cotton Batting Institute, Textile Waste Association, National Cottonseed Products Association, and the Foundation for Cotton Research and Education, research is being conducted to improve the bulk resilience and cohesion of cotton batts so they can better meet the serious competition from polyurethane foams and foam rubber in mattresses and other padding applications in the furniture and automobile industries.

Excellent, chemically treated cotton batts having improved dimensional stability coherence and resilience have been produced experimentally in the pilot plant. In the process employed, commercially available water-soluble resin and latex combinations are sprayed onto webs from a sample card during batt formation and the formed batts are then subjected to curing. A blend containing 60%

cotton linters and 40% textile waste in the batt gave the best products, and was used in most of the experimentation.

It has also been found that cotton batting treated with melamine formaldehyde resins and a latex can be molded into products having resilience and dimensional stability. The experimental products made to date appear very promising. They should have applications in head liners, bucket seats and crash pads in the automobile industry, and as padding in contoured furniture.

Effort is being directed toward further screening of resins and latexes for suitability in making the batts, as well as chemical methods of crimping or kinking the fibers and means of achieving greater randomization of the fibers in the web. (S2 1-181).

F. Effect of Yarn and Fabric Construction on the Physical Properties of Chemically Treated Cotton Fabrics.

1. Effect of Fabric Structure on Chemically Treated Fabrics. Chemical, resin or combination treatment of cotton roving could provide new and improved properties useful in such applications as heavy woven products, knitted paddings, tightly twisted or plied yarns, and thermoplastic yarns. Engineering studies have been initiated to determine the feasibility of such treatments.

A new type apparatus has been developed which appears promising for rapidly and uniformly wetting conventionally packaged roving. Using the apparatus, wetting tests on roving packages indicated the need for a more versatile processing unit designed to operate under controlled conditions over a wide range of processing variables, and the need for reducing package deformation during processing. The first unit of a three package processing unit proposed to achieve this has been designed, fabricated and installed. Encouraging results have been obtained with it.

Roving packaged on stainless steel tubes has been rapidly and completely wetted at a controlled preselected level of wet pick-up of 100-150 per cent; and it has been possible to duplicate the selected wet pick-up level. This has been accomplished with only slight visual package distortion. Complete uniformity of wetting has not yet been achieved, but it is believed that by slight modification of the processing procedure this can be accomplished. Once the feasibility and practicability of the process has been established, products where bulk (low density) or, conversely, high density, is required will be produced for evaluation. (S2 1-184).

Although crepe fabrics can be made from cotton, silk, wool, and other type yarns, most of the crepe fabrics manufactured today are made from continuous filament rayon fibers. The inherent property of rayon to swell 100% from the bonedry to the wet state is used to advantage in the finishing operation where the swelling action during wet processing causes the high twist yarns to shrink and when tension is released the fabric will relax and give the desired crepe effect. Improvements in cotton's swelling properties, and in strength characteristics of cotton crepe yarns when subjected to the necessary high twist, are needed to make cotton more suitable for use in crepe fabrics.

Satisfactory progress has been made at the Philadelphia College of Textiles and Science in contract research whose aim is the designing and developing of acceptable cotton crepe apparel fabrics by using new and improved methods of yarn and fabric structures, chemical modifications and finishing treatments.

Experimental yarns were spun from a series of long staple cottons selected on the basis of fiber length, fineness and elongation, and some of the yarns have been woven into a narrow fabric as filling for evaluation as to their crepeing qualities. The mechanical crimping of yarns made by knitting the yarns into fabric, resin treating the fabric, curing the resin, and then unraveling the fabric appears promising for producing good crepe yarns. Reagents for enhancement of the water swelling of cotton yarns are also being investigated to improve crepeing properties. (S2 1-157(C)).

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AREA NO. 6 - COTTONSEED PROCESSING AND PRODUCTS

Problem. Cottonseed products, currently approximately two billion pounds of oil and 2.5 million tons of meal derived from the annual domestic production of cottonseed, face increasing competition for markets. For its chief market, edible products, cottonseed oil must compete with other vegetable oils and animal fats. The nation's capacity for producing these oils and fats is so great that supplies can be expected to exceed both domestic and foreign demand for some time to come. Cottonseed meal, used chiefly as a protein supplement in feeding ruminant animals, faces serious competition from synthetic urea and other supplements. Improvements in the quality and utility of cottonseed oil are needed to retain present and open new markets for the currently large and possibly greater future production.

As an illustration, there is a discrimination in the markets against 25% to 50% of the current production of cottonseed oil due to the presence of reddish colors that are not removed by present commercial refining, bleaching and deodorizing methods. It is essential that information be developed on the chemistry of the pigments responsible for the off-colors, and that practical means be found to eliminate them and thus upgrade the oils, particularly for use in margarine and shortening. Additional information is needed urgently on the chemical and biochemical properties of cyclopropene fatty acids in cottonseed and means of converting them, if found necessary, into physiologically inert forms. New types of modified fats, such as polyester and polymeric fats, need to be developed from cottonseed oil for applications in the fields of edible and inedible coatings, waxes, resins, plasticizers, and lubricants. Cocoa butter-like fats and other confectionery fats derived from cottonseed oil could also provide new markets for large quantities of oil. Fundamental information is needed on hydrogenation to permit production of improved plastic fats. Other areas in which markets for cottonseed oil need to be developed through research include fat emulsions for intravenous feeding, edible emulsifiers, and fatty acid amides and derivatives for use as plasticizers, plastic foams and other industrial products. Improvement in the quality and nutritive value of cottonseed meal is needed so that it can better compete with other protein feed supplements. Additional information is needed on the physiologically active constituents of the meal responsible for egg abnormalities, swine mortalities and growth abnormalities of young animals that limit cottonseed meal's usefulness in poultry and swine rations. Processing methods must be devised for the commercial production of meals that can be fed to broilers, laying hens and swine, safely and without restriction. In order to lay the necessary groundwork for advances in cottonseed research on food, feed and industrial products and processing technology, additional fundamental information is also needed on the chemical composition and properties of cottonseed and of various cottonseed products.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists, physical chemists, analytical chemists, biochemists, chemical engineers, physicists, bacteriologists and microbiologists engaged in both basic and applied studies on cottonseed and its products to develop new or extended uses for these materials. Research to develop fundamental information on the chemical composition and properties of cottonseed products is conducted at New Orleans,

Louisiana, as a basis for efficient applied research in the fields of food, feed and industrial products from cottonseed. One phase of the work, research on cottonseed oil pigments, is supported in part by a Research Associateship maintained by the National Cottonseed Products Association at the Southern Regional Research Laboratory, New Orleans, Louisiana. Additional research on chemical composition and physical properties is carried out under contract at the University of Tennessee, Knoxville, Tennessee, on investigations of gossypol esters and mild oxidation products of gossypol and gossypol derivatives; and at the University of Illinois, Urbana, Illinois, on investigation of the chemical and physical properties of cyclopropene fatty acids in cottonseed. New and improved food products and processing technology are developed in research conducted at New Orleans, Louisiana. Research on confectionery fats is cooperative with the National Confectioners' Association who maintain a Fellowship at the Southern Regional Research Laboratory, New Orleans, Louisiana in partial support of the work, and evaluate promising research products. The Office of the Surgeon General supports research to develop fat emulsions for intravenous alimentation. This research is conducted in cooperation with the Louisiana State University Medical School, New Orleans, Louisiana, and several other research groups. A visiting research scientist sponsored by the government of Brazil assists with phases of the research on fats and oils, particularly that involving cyclopropene acids of cottonseed oil, at the Southern Regional Research Laboratory. Informal cooperation is maintained with industry in connection with the research on new and improved food products and processing technology. Research is carried out at New Orleans, Louisiana to develop new and improved feed products and processing technology for cottonseed. The National Cottonseed Products Association maintains a Fellowship at the Southern Regional Research Laboratory, New Orleans, Louisiana to partially support research on physiologically active constituents in cottonseed meals that adversely affect the utilization of the meal as a protein supplement in nonruminant feeding. The Pharmacology Laboratory at the Western Regional Research Laboratory, Albany, California, cooperates by conducting small-animal studies to determine the physiological and pharmacological effects of cyclopropene acids. Other animal tests in connection with the overall research program are conducted through the cooperation of nutritionists in State Agricultural Experiment Stations and the Animal Husbandry Research Division. In research directed toward providing a basis for the ultimate commercial production of cottonseed meals that can be fed to swine and poultry without restriction, as well as to ruminant animals, cooperation is maintained with the National Cottonseed Products Association, members of the cottonseed industry and nutritionists in public and commercial agencies. Because of the possible implications of this research to the utilization of cottonseed meals as protein sources in human nutrition, UNICEF sponsors two visiting foreign research scientists stationed at the Southern Regional Research Laboratory to assist with certain phases of the research. Research to develop new and improved industrial products and processing technology is conducted at New Orleans, Louisiana. Informal cooperation is maintained with industrial firms for the evaluation of promising research products for specific end uses. Additional research on new and improved industrial products is being carried out under contract at the University of Arizona, Tucson, Arizona, on the polymerization of reactive chemical intermediates derived from cottonseed oil and other agricultural materials to produce polymers having potential industrial utility.

Other research on chemical composition and physical properties is in progress under grants of P.L. 480 funds to the following foreign institutions: British Food Manufacturing Industries Research Association, Leatherhead, Surrey,

England, for fundamental studies of the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components (2.0 professional man-years); and University of Bombay, Bombay, India, for a study of the relationship of substituent fatty acid groups on the physical properties of diacid triglycerides of palmitic and stearic acids as a means of increasing the utilization of cottonseed oil for food and industrial purposes (3.3 professional man-years). Additional research to develop new and improved industrial products and processing technology is in progress under grants of P.L. 480 funds to the following foreign institutions: Institute for Research on Oils and Fats, Paris, France, for investigation of the preparation and properties of alkyl aryl ketones and their derivatives from vegetable oils for industrial applications (3.0 professional man-years); and University of Montevideo, Montevideo, Uruguay, for research on the preparation, characterization and evaluation of derivatives of gossypol for use as biologically active materials, ultraviolet absorbers and other products (3.4 professional man-years).

The Federal in-house scientific effort devoted to research in this area totals 40.8 professional man-years. Of this number 12.1 is devoted to chemical composition and physical properties, 16.1 to new and improved food products and processing technology, 10.1 to new and improved feed products and processing technology, and 2.5 to new and improved industrial products and processing technology. The contract research involves an additional 1.5 man-years, 0.8 being on chemical composition and physical properties and 0.7 on new and improved industrial products and processing technology. P.L. 480 research totals 11.7 man-years, of which 5.3 is on chemical composition and physical properties and 6.4 is on new and improved industrial products and processing technology.

The following lines of work were terminated during the year: (1) Investigations of the reactions of gossypol to aid the development of improved cottonseed meal and oil of enhanced value (under chemical composition and physical properties); (2) Development of new hydrogenation techniques for cottonseed and peanut oils to produce improved edible fat products and intermediates for industrial uses (under new and improved food products and processing technology).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 0.3 professional man-years effort in this area, all under the subheading new and improved food products and processing technology. Chemical analysis and amino acid content determination have been made as a measure of nutritive value.

Industry and other organizations conduct a sizable amount of research in this area, the estimated annual expenditures being equivalent to approximately 75 professional man-years. Of this total about 12 man-years is on cottonseed processing research, 35 man-years on cottonseed oil processing research, and 28 man-years on developing new and improved cottonseed oil products.

Several engineering companies and processors are engaged in the development of new and improved processes and equipment for improving the efficiency of processing cottonseed, and for improving the feeding quality of the meal and the quality of the oil. The modern processing plants are the result of composite research effort and consist of elements of different manufacture, with

the trend being toward solvent extraction. The processors, through the National Cottonseed Products Association, support research through fellowships at the Southern Utilization Research and Development Division and grants to universities on improvement of cottonseed products, principally meal quality and oil color. Industry research is being implemented and stimulated through the results of basic and applied investigations at the Southern Utilization Research and Development Division.

Known research effort on processing of cottonseed oil is largely conducted by firms for their own use and is aimed at developing and improving methods for refining, bleaching, deodorizing, winterizing, and hydrogenating the oil. Engineering firms are developing improved processes and equipment. Processes receiving particular attention include solvent refining and bleaching, solvent winterization, deodorization, and continuous hydrogenation. Research toward finding better hydrogenation catalysts is underway. One large company is reviewing all of the conventional oil processing operations with a view of improving them. The National Cottonseed Products Association supports a Research Associateship at the Southern Utilization Research and Development Division on the identification and removal of the coloring substances in off-colored oils.

Research is directed by commercial firms toward developing new and improved products such as new plastic or semi-solid fats, cocoa butter-like and other confectionery fats derived in part from cottonseed oil, emulsifiers and other surface active agents, and new esters of various polyols and fatty acids. Glycerides containing cottonseed oil fatty acids and short-chain dibasic acids, developed at the Southern Utilization Research and Development Division, are now being investigated by one large manufacturer of fatty products. The National Confectioners Association sponsors a Fellowship at the Southern Utilization Research and Development Division and information developed relative to the making of new confectionery fats from cottonseed oil is disseminated by their Research Advisory Committee to oil processors and confectioners. Several companies are conducting relatively fundamental research, either in their own organizations or under contract, including research on glyceride configuration and physiological behavior of cottonseed oil and its products. Additional information on chemical composition and fundamental physical properties is desired but usually research in this area cannot be justified on the basis of immediate profit to the companies undertaking it. The industry looks to the Southern Utilization Research and Development Division, and similar organizations, for obtaining such basic information. Research for nonfood uses of cottonseed oil is being done at a low level, probably because cottonseed oil has historically been purchased and processed by a segment of the food industry which is not likely to search for nonfood uses. A plasticizer from cottonseed oil fatty acids, developed in the Southern Utilization Research and Development Division, is being evaluated commercially.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Chemical, Physical, and Biological Properties and Structural Factors of the Proteins. The composition, properties, structural factors and reactions of oilseed proteins and associated materials are being investigated as a basis for development of new concepts and possibly new uses for oilseed proteins, including cottonseed protein. Major areas of recent research have included

studies of seed globulins, of their subcellular distribution, and of a specific group of seed proteins, the lipases. Since peanuts were found to be an especially suitable experimental material and employed for much of this fundamental research on seed proteins, the report of progress in the research is given in Area No. 7, "Peanuts Processing and Products."

2. Chemical and Physical Properties of Pigments and Minor Constituents

Including Cyclopropene Fatty Acids. Additional information was developed concerning the problem pigments of off-color cottonseed oils as a possible basis for improving the color and quality of these type oils. Two major pigment fractions from a model system (refined and bleached cottonseed oil anaerobically reacted with gossypol) were resolved chromatographically through the use of powdered cellulose and silicic acid columns. Each of these fractions was further separated into two components by means of countercurrent distribution. Purification and characterization of the four components is in progress. One has yielded a homogeneous, major fraction in which there is evidence for the presence of esters. Indications are that an ester interchange reaction occurs and the problem pigments may be partial esters of gossypol or anhydrogossypol. A Research Associate of the National Cottonseed Products Association assists with the research. (S4 1-96).

In continued contract research at the University of Tennessee on the chemistry and reactions of gossypol, (1) twenty new gossypol anils were prepared, (2) desapogossypol was synthesized and converted to several acetate derivatives, (3) apogossypol hexallyl ether was made and studied, (4) 1, 4-binaphthoquinones derived from gossypol were found to undergo epoxidation at the 2, 3 positions, (5) three crystalline oxidation products of gossypol were isolated, (6) an unusual mono-Diels-Alder adduct between anhydrogossypol and cyclopentadiene was discovered, and (7) evidence was obtained for an interchange reaction between a gossypol anil and an amine. A variety of biological activity tests on gossypol derivatives failed to indicate any chemotherapeutic use for gossypol or its derivatives. The contract project has been terminated, and new contract research initiated at the University of Tennessee involving investigations of gossypol esters and of mild oxidation products of gossypol and gossypol derivatives to develop information needed to aid the production of cottonseed meals and oils of the highest quality (S4 1-73(C); S4 1-103(C)).

Several approaches have been found which look promising for the development of quantitative analytical methods for determination of cyclopropene acids in cottonseed products. Among the promising methods under further development are the following: (1) a modification of the conventional qualitative Halphen color test method, (2) a modified hydrobromic acid titration method, (3) a procedure based on chlorine analysis after treatment with aqueous hydrochloric acid, and (4) a method involving infrared absorption measurements on the hydrochloric acid-treated materials. These methods are being examined as to precision, range of application, and influence of interfering substances. Recently initiated contract research at the University of Illinois to investigate chemical and physical properties of cyclopropene fatty acids in cottonseed should aid in the development of such quantitative methods of analysis, and in improving cottonseed meal and oil. (SG-0-1; S4 1-104(C)).

3. Chemical and Physical Properties of the Oil and Fatty Acids.

Evidence has been obtained that the chemical and physical properties of cottonseed oils bleached with normal activated alumina are almost identical with those for oils bleached with the conventionally used Fuller's earth. In the laboratory

experiments it was found that alumina bleaching does not impair oil stability or induce significant amounts of isomerization in the oil. These are important findings for possible commercial use of alumina for bleaching off-color cottonseed oils. The spent alumina can be reactivated by simple incineration at 500°-550°C., and reused repeatedly without loss of its effectiveness as a bleaching agent and with little loss of alumina. It was also observed that if the alumina is first treated with aqueous sulfurous acid, the capacity of the alumina to remove green pigments, as well as the problem pigments of off-color oils, is enhanced and the Halphen test (cyclopropene acids) is negative. No adverse effect on properties of the bleached oils has been observed to date. (S4 1-96).

New systematic solubility data on long-chain fatty acids and their derivatives in various industrial solvents were obtained to develop correlation methods and information fundamental to research on industrial utilization of fatty acids from cottonseed oil and other vegetable oils. The pure cyclohexylamine salts of stearic, palmitic, myristic, and lauric acids were prepared and solubility curves for the salts in benzene were obtained. Solubility curves were also determined for the cyclohexylamine salts of capric and heptadecanoic acids in benzene and in acetone to complete the series in these two solvents. With the exception of the heptadecanoic salt, as anticipated, the results show good agreement when correlated by means of isotherm and isopleth correlation graphs. The existence of two polymorphic forms of elaidic acid was confirmed by obtaining the solubility curves of both modifications in methanol down to -10°C. It is planned to investigate the solubilities of the cyclohexylamine salts of the various fatty acids in methanol. The data will be correlated to provide a basis for prediction of solubilities. (S4 1-88).

In P.L. 480 research at the British Food Manufacturing Industries Research Association, studies are in progress on the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components. Cottonseed oils produced from seed grown under various environmental conditions may differ appreciably in the amounts of the component fatty materials they contain; this, in turn, affects the yields obtained and the characteristics of the finished product when these oils are processed to obtain salad oil. The crystallizing behavior and the influence of oil composition of a number of cottonseed oils of different environmental origins are being studied under various processing conditions. The study will provide data useful in the selection and processing of cottonseed oils for the commercial production of improved salad oils in optimum yields. (UR-E29-(40)-26).

B. New and Improved Food Products and Processing Technology

1. New Edible Oil Products Including Confectionery Fats, Food Coatings and Other Specialty Products. Further research was done on the production of a cocoa butter-like fat, principally to devise suitable procedures to remove the small amounts of high-melting, trisaturated glycerides whose presence in earlier batches of the product was deemed undesirable. It was found that the trisaturated glycerides may be conveniently removed from cocoa butter-like fats by special tempering procedures and then filtering or by crystallization from a 1:1 solution of the fats in petroleum ether. Dilatometric examination of the purified, deodorized fats revealed that a well-tempered sample contained only 0.7% liquid oil at 15°C. and 96.3% at 35°C., which is very desirable.

Research was conducted on the molding characteristics of cocoa butter to develop fundamental data for improving the demolding performance of synthetic cocoa butter-like fats. High solids content at time of molding resulted in poor contraction. Further, it was established that to obtain proper contraction on solidification of cocoa butter, seeds of the highest melting polymorphs should be present and solidification and tempering should be carried out between 14° and 16° C. In the course of the work, a procedure was developed for determining the maximum linear contraction of cocoa butter and cocoa butter-like fats on solidification.

Films of cocoa butter were produced which have much improved resistance to permeability to water vapor than previously prepared films. A synthetic cocoa butter-like fat, however, gave films about five times as permeable as the best cocoa butter films.

In the course of laboratory work on the fundamental properties of cocoa butter and other confectionery fats, it was discovered that cocoa butter, the Southern Division's cocoa butter-like fat, and some other fats can be transformed directly into the stable crystal form by extrusion of the unstable crystal forms through small orifices under high pressure. The transformation has been found to be due to mechanical working under these conditions and not an effect of high pressure alone. This new process could result in a simplified and more direct process of manufacturing chocolate in that the process could be truly continuous and the use of tempering kettles could be eliminated. Good progress has also been made in determination of dilatometric and other physical properties of the individual glyceride components of the confectionery fats.

A promising new approach to making cocoa butter-like fats and other special fats has been discovered. It involves direct esterification of diglycerides (of palmitic and stearic acids, for example) with oleic acid in such a manner that interesterification doesn't occur, although some isomerization of the diglycerides occurs prior to the esterification. Cocoa butter-like fat products having good melting characteristics were obtained in the laboratory in high yield by this procedure which will be investigated further. The research on confectionery fats is supported in part through a fellowship sponsored by the National Confectioners' Association. (S4 1-91).

In continued research on new polyester products from cottonseed oil, work was completed on a series of fatty acid esters of amylose containing oleic, linoleic and the even-numbered saturated fatty acids C₂ through C₁₈. The degree of acylation was found to be inversely proportional to the chain length of the acyl group. Intrinsic viscosities decreased as the chain length increased, a reflection of the changing nature of the products rather than the degree of polymerization of the amylose. The effects of chain length and degree of unsaturation were determined for such properties as softening point, hardness index, density, tensile strength, percent elongation, and permeability to water vapor. Results indicate that it is possible to tailor-make film-forming polyesters with specific properties by varying the length of substituted acyl group and the extent of unsaturation.

Recent research has been directed toward devising new and more economical methods of preparing glycerides and dibasic acid-containing polyester fats. Some preliminary experiments indicated that only one-half of a dibasic acid can be esterified effectively with a diglyceride. It should be possible to esterify the half-ester with hydroxyl groups as in mono- and diglycerides, fatty alcohols, or phenols. Other investigations have been concerned with the

preparation of specific diglycerides by controlled esterification. Preliminary experiments with 1-monostearin and oleic acid indicate that simple esterification predominates, although there is some ester interchange, and the process should be valuable for preparing diglycerides. Further work is underway to obtain a more complete understanding of the mechanism of the esterification.

In another phase of the research, involving investigation of the fungistatic effect of fatty acids and fats derived from cottonseed oil, compounds containing caproic acid were synthesized and tested for fungistasis by a recently developed method for quantitative estimation of fungistasis by fats. Tri-caproin has been found to have some fungistatic effect on certain microorganisms. (S4 1-90).

Research supported by the Office of the Surgeon General was continued on the development of emulsifiable oils and fats for use in fat emulsions for intravenous alimentation. An improved fat emulsion (675) was developed and used successfully for infusions on dogs. When close analytical control of the purity of the emulsifying system is maintained, the test animals have shown no abnormal effects, such as development of anemia or pulmonary effusions, as observed with previous emulsions. The principal emulsifying agent in this emulsion is a stearate ester of polyethylene glycol, the latter a mixture of polymers of several molecular weights. Analytical control methods have been set up for the emulsifiers so that successive batches of materials will meet critical specifications.

Recently, a more homogeneous and improved primary emulsifying agent has been synthesized in the laboratory by esterifying purified palmitic acid with a molecularly distilled fraction of polyethylene glycol. The new emulsifier has also been prepared by a commercial firm, and following purification has proven comparable to the laboratory preparation. The use of this primary emulsifier (polyethylene glycol palmitate) in conjunction with a non-acetylated secondary emulsifier in a fat emulsion has given significant improvements in the physiologic response of dogs administered the emulsion. The physiologic advantages are obtained with no sacrifice of desirable physical properties of the emulsion. The emulsion (695) has now been prepared commercially, extensively evaluated on animals, and is undergoing clinical evaluation.

Synthetic triglycerides are being prepared for use in a study of the cause and nature of liver pigmentation resulting from prolonged administration of all cottonseed oil emulsions irrespective of emulsifier system. Methods of modifying cottonseed oil to eliminate its response to the Halphen color test are also being investigated in connection with use of the oil as the lipid source of emulsions. (SG-0-1).

2. Processing Technology Related to Improved Oil Products, Including Modifying or Eliminating Cyclopropene Acids in Cottonseed Oil. Engineering studies were initiated to develop a commercially feasible process for preparing cocoa butter-like fats based on chemical laboratory research. Approximately 100 pounds of crude cocoa butter-like fat (No. 5) were produced in the pilot plant. An increase in yield of about 25% was obtained, presumably due to a new method of adding the catalyst. The product was further purified, yielding 77 pounds of a cocoa butter-like fat exhibiting improved melting behavior due to removal of small amounts of saturated fats during the purification. Confectioners are evaluating the fat. Revised costs for producing cocoa butter-like fats from cottonseed oil have been prepared, reflecting the

effect of recent changes in process development to improve product quality. Future work will place emphasis on studies of the effect of short crystallization time, an important consideration in the commercialization of a continuous process for producing cocoa butter-like fat. (S4 1-101).

Development work on bleaching off-color cottonseed oils with activated alumina is in progress to devise a commercially practical bleaching process based on the use of this highly active adsorbent. Laboratory scale alumina bleaching tests indicated that combining alumina bleaching with deodorization was not as effective in reducing oil color as bleaching alone. Batch type bench scale equipment to permit rapid evaluation of process variables and provide necessary process design data was designed and fabricated. Preliminary tests with the equipment showed it would be necessary to find a commercial source of an alumina having the correct particle size distribution for rapid filtration from the oil as well as good bleaching power; and a method of removing green color from the oil would be needed. A subsequent extensive series of tests with a variety of aluminas has shown that none of the commercial aluminas received up to the present time have the required properties of maximum bleaching activity and desired particle size. The preparation of such aluminas in commercial quantities may present special problems. The use of small amounts of carbon (0.1% of oil weight) mixed with alumina in pilot-plant runs has proved to be a solution to the problem of reducing green color. Results with five commercial oils show that rerefining followed by natural earth bleaching yields bleached oils of appreciably lighter colors than can be obtained by bleaching with four percent of alumina. Oil losses by rerefining followed by earth bleaching were slightly lower than the losses by alumina bleaching. Preliminary estimates based on available pilot-plant data indicate that the cost of bleaching off-color cottonseed oils with alumina should be comparable to the cost of present commercial procedures (rerefining, followed by earth bleaching) for processing these oils. The research is now being concentrated on improving filtration rates either by preparing aluminas of suitable particle size or employing filter aids, to make the process commercially feasible. (S4 1-92).

Studies of the hydrogenation process for modification of vegetable oils are being made to develop new hydrogenation techniques for cottonseed and peanut oils that will enable the production of new and improved edible fat products. Further work on hydrogenation of methyl esters of fatty acids using the Adkin's No. 5 nickel catalyst showed that it was not possible to reproduce with any precision the activity of this catalyst for the methyl esters. Factors such as the amount of aluminum present in the catalyst, and the support material for the catalyst, may be responsible.

The minimum concentration of palladium-on-carbon catalyst which would not cause an appreciable decrease in the hydrogenation rate of a triglyceride oil in solvent was determined, and the effect of temperature in the range from 30° to 55°C. was studied. In other experiments with this catalyst it was established that without use of solvent, neither the least practical amount of catalyst nor very low hydrogenation temperatures were effective in reducing the amount of trans isomers formed to an acceptable level. However, the use of solvent resulted in a significant reduction of the trans isomer content of the product.

In recent research the important discovery was made that position of the unsaturated acyl groups on the glycerol molecule does not influence

hydrogenation rate. A method has also been developed for preparing nickel catalysts having greater activity and stability, capable of producing improved hydrogenated fats with lower trans isomer content.

Initial experiments on the use of hydrogenation in modifying or eliminating the physiologically active constituents, cyclopropene fatty acids, in cottonseed oil indicate that these acids can be removed by hydrogenation under conditions which do not hydrogenate the linoleoyl groups or oleoyl groups or produce positional isomers of these groups. This promising approach will be investigated further. (S4 1-84; S4 1-102).

C. New and Improved Feed Products and Processing Technology

1. Basic Research to Improve Nutritive Value of Cottonseed Meal for Laying Hens and Swine, Including Investigations of Cyclopropene Acids in the Meal.

Much of the confusion in the literature relating to the discolorations in stored shell eggs from cottonseed meal-fed hens has been cleared up through the discovery that the chromogen in the yolk is a pH indicator, and that the brown color develops in the yolk only when the yolk pH is abnormally high. The physiologically active gossypol derivatives in cottonseed meal responsible for the brown chromogen in the yolks are tightly bound in the meal and are not removed by any one of several solvents. The Halphen-positive fatty acid of cottonseed glycerides was isolated and identified as 2-octyl-1-cyclopropene-1-heptanoic (malvalic) acid. The presence of this acid in cottonseed meals fed to laying hens accentuates the yolk color problem because the effect of Halphen acid on the permeability of the vitellin membrane fosters an abnormally rapid increase in yolk pH while the eggs are in cold storage. A Fellow of the National Cottonseed Products Association assisted with this research.

Feeding tests have confirmed the high nutritive value of hexane-acetone-water extracted cottonseed meals and also confirmed the previous conclusion that total gossypol and lysine, but not free gossypol, are of paramount importance in determining the nutritive quality of cottonseed meal. In other research a heat labile antinutrition factor, extractable with hexane-acetone-water solvent mixture, has been found in cottonseed. This suggests that the nutritive quality of cottonseed meal may be further improved.

It has also been found that cottonseed products high in protein and low in crude fiber can be obtained through air separation of ground cottonseed meal. Preliminary analyses indicate that the protein-rich fraction from the air separator is also richer in lysine. Use of this technique offers a possible approach for producing meals of high protein and low fiber content for broiler and swine feeding.

The high-lysine (5.2%) protein fraction from glandless cottonseed (approximately 25% of the total protein) is glyco-protein; color reactions indicate the presence of amino sugars. The protein fraction is rich in sulfur and poor in phosphorus. Exploratory experiments to determine the importance of processing on the several amino acids in cottonseed meals show that epsilon free amino lysine is the most labile amino acid. Studies with dinitrofluorobenzene treated meals have formed the basis for more rapid and more reliable methods for available lysine assay in oilseed meals. Recent investigations of ion-exchange chromatography of amino acids in hydrolyzates of cottonseed proteins prior to and following dinitrofluorobenzene treatment

of the cottonseed meal have shown that this method can be used for quantitative determination of available lysine. A UNICEF-sponsored research scientist participated in this research.

Basic studies are in progress on the fractionation of the alcohol-salt soluble cottonseed proteins to determine the nature of the growth stimulating factor that appears to be present in cottonseed. Protein fractions have been isolated which are rich in the basic amino acids, lysine and arginine; high in the acidic amino acid, glutamic acid; and exceptionally high in the sulfur amino acids, cystine/cysteine and methionine, as compared with the whole cottonseed meal. Accompanying this is a sharp decrease in the neutral amino acid content and a complete inversion of the tyrosine/phenylalanine ratio. Preliminary evidence indicates that the proteins from glandless cottonseed may be significantly richer in threonine and valine than those from glanded seed.

The usefulness of Tetrahymena pyriformis W. is being explored in a continued effort to find a rapid and economical means of evaluating nutritive quality of cottonseed meals.

Basic studies of the gossypol-amine reaction are yielding information which may point the way to a reversal of the gossypol-lysine reaction in meals, thereby improving their nutritive quality.

Cottonseed oils bleached with sulfurous acid-treated alumina to give a negative Halphen test, as well as conventional oils, are being used in tests on chicks and laying hens to obtain data on the physiological effects of malvalic acid present in cottonseed. The results will also be of importance from the standpoint of use of alumina for bleaching cottonseed oils. (S4 1-95; S4 1-97).

2. Processing Technology Related to Improved Meals Including Removal or Inactivation of Cyclopropane Acids. Based on laboratory findings which indicated that processing cottonseed with a solvent mixture of hexane-acetone-water could be employed to produce improved cottonseed meals suitable for swine and poultry feed, engineering studies were initiated to develop such a process suitable for use on a commercial scale. Two approaches showing considerable promise have been investigated on a pilot-plant scale.

In one of these approaches the development work is directed toward adaptation of existing commercial basket extraction plants to the mixed solvent process with the minimum modification of, or use of, additional equipment. A modified process is being sought that provides optimum combination of extraction efficiency for oil and gossypol, with satisfactory plant operation in the various steps of extraction, meal desolventizing, oil desolventizing, mill-site oil or miscella refining, solvent rectification, reconstitution and continuous regulation of solvent composition. Plant capacity, solvent losses, loss of product weight due to solution of non-lipids in the mixed solvent, oil quality and over all costs are also factors being considered in the choice of mixed solvent composition and process features. In pilot-plant runs using an 8-cell countercurrent basket extractor, the guide lines for total gossypol (0.30%) and epsilon-amino-free lysine (4.0 grams per 16 grams of nitrogen) were consistently met and for free gossypol (0.03%) and lipids (0.5%) were approached at extraction times of 120 minutes and ambient

temperatures. However, extraction rates for oil and gossypol will have to be improved to achieve guide line values in about 40 minutes corresponding to commercial practice. A UNICEF-sponsored research scientist assists with this research.

The second approach has involved use of a 10-stage countercurrent continuous extraction with a vibrating screen separator (Sweco). Processing experiments have shown this type of extraction using hexane-acetone-water solvent mixture to be practicable---fines and screenings can be handled continuously by recirculating them at suitable points in the extraction cycle. Pilot-plant scale recovery and refining of oils from mixed solvent-extraction indicated the procedure to be practical on a larger scale. Meals and oils of superior quality were obtained.

UNICEF is conducting comprehensive nutritional tests on some mixed solvent-produced cottonseed meals. Preliminary reports indicate protein efficiency ratios comparable to those obtained for toasted soy products. (S4 1-94; S4 1-95).

D. New and Improved Industrial Products and Processing Technology

1. Basic Research to Develop New Reactions and Products Suitable for Industrial Use. Long-chain fatty amides and derivatives are being prepared, characterized, and evaluated as plasticizers, stabilizers, polyurethane foams, and for other industrial uses. The selectively hydrogenated cottonseed oil fatty acid morpholide developed in earlier research has been successfully prepared in quantity in the pilot plant. This plasticizer for vinyl plastics and cellulose triacetate is undergoing evaluation tests by industrial firms.

The morpholide of selectively hydrogenated cottonseed acids has been found to be an effective compatibilizer for incompatible fatty acid type plasticizers. It is also an effective compatibilizer for hydrocarbon type extenders in vinyl chloride and vinyl chloride copolymer resins. Cost aspects of the morpholide are thereby improved; and the extenders also give the beneficial effect of reducing soapy water extractability. By condensing partially epoxidized cottonseed fatty acids with morpholine, an efficient plasticizer and particularly good stabilizer for vinyl chloride has been made.

In other work it was established that the morpholide of parsley seed fatty acids is a highly efficient compatible plasticizer for vinyl chloride; and indications are that the morpholide of dimer linoleic acid might be a satisfactory vinyl plasticizer in such uses as floor tiling. Preliminary experiments indicate that dimerization may be preferable to hydrogenation in the preparation of cottonseed morpholide plasticizers.

Two crystalline forms of elaidic acid (freezing points, 43.7° and 44.8°C.) have been isolated in the course of the research. This is the first trans-alkenoic acid known to occur in two polymorphic forms. Binary freezing point diagrams for the systems oleic acid-petroselinic acid, oleic acid-petroselaidic acid, oleic acid-elaidic acid, elaidic acid-petroselinic acid, and elaidic acid-petroselaidic acid were constructed and all found to be of the simple eutectic type.

Additional N,N-disubstituted long-chain fatty amides have been prepared, characterized, and evaluated as polyvinyl chloride plasticizers.

N,N-bis(2-acetoxyethyl)oleamide and N-oleoylpiperidine compare favorably with other acceptable plasticizers, giving brittle points of -44° and -47°C . and volatility losses of 0.80 and 1.17%, respectively, as compared to -31°C . and 1.50% for dioctyl phthalate and -55°C . and 6.00% for the more expensive dioctyladipate. A simplified synthesis of the bis compound has been found which should reduce cost to a realistic competitive level. Some fifty long-chain amides and substituted amides have been submitted to screening for antibacterial activity. A number of them show exceptional promise as antimycotic agents, being effective against a broad spectrum of organisms. The research effort will continue on other fatty amide derivatives, particularly substituted piperidines. (S4 1-99).

Contract research at the University of Arizona is directed toward development of new industrial products by polymerization of reactive chemical intermediates derived from selected agricultural materials, including cottonseed and other vegetable oils. Emphasis is on polymers for use as elastomers, plastics, thickening agents, and protective coatings. Copolymers prepared by copolymerizing vinyl chloride with vinyl 12-ketostearate, with vinyl 4-ketostearate, and with vinyl 9(10)-ketostearate have been milled into plastic form to evaluate the effect of the keto group on internal plasticization. The keto compounds were found to have no advantage in this respect over vinyl stearate. The polymerization of vinyl esters of other fatty acid derivatives has been studied, including the preparation of copolymers of vinyl chloride with vinyl tetrachlorostearate and with vinyl dichlorostearate, and homopolymers of the latter compound and other monomers. Evaluation of the properties of the polymers is in progress. (S4 1-89(C)).

P.L. 480 research at the Institute for Research on Oils and Fats is concerned with the preparation and properties of alkyl aryl ketones and their derivatives from vegetable oils for industrial applications. This research has produced chemical derivatives of the alkyl aryl ketone type that have potential utility in such industrial products as fungicides, lubricants, plasticizers, and surface-active agents. (UR-E9-(00)-29).

The preparation, characterization, and evaluation of derivatives of gossypol having potential industrial utility is in progress under P.L. 480 research at the University of Montevideo. Since gossypol is a very reactive polyfunctional polyphenolic pigment which can be obtained in good yield from by-products of the refining of cottonseed oil, it is currently being explored as an intermediate in the preparation of compounds useful in pharmaceuticals, insecticides, fungicides, ultraviolet absorbing or screening agents, and similar materials. (UR-S9-(40)-2).

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AREA NO. 7 - PEANUTS PROCESSING AND PRODUCTS

Problem. Peanuts constitute a major cash crop in the Southern States and are in surplus. Because of the high price of peanuts in the United States, peanuts are used almost exclusively (more than 80 percent of the crop) in foods such as peanut butter, confections, and roasted and salted nuts. New type food products and improvement in the quality and uniformity of existing products are needed to increase consumer acceptance and extend markets; the average per capita consumption has been rather stable since World War II. The increased trend toward mechanical harvesting has necessitated the use of artificial means for curing and drying peanuts, with the result that processed peanuts and peanut products do not always possess the same desirable flavor and physical properties as peanuts which have been cured slowly in the field. Information is needed as to the physical and chemical characteristics of those chemical constituents in peanuts which affect the properties of processed products as a basis for developing new or improved products and processing procedures. Fundamental studies of peanut protein and associated materials could similarly lead to the development of new concepts and new uses.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists, biochemists, and chemical engineers engaged in both basic and applied studies on peanuts and its products to increase consumer acceptance and extend markets for peanuts. Research to develop basic information on the chemical composition and properties of peanuts, its constituents, and processed peanut products is carried out at New Orleans, Louisiana. Fundamental investigations of peanut proteins and associated materials are conducted to form the basis for developing new concepts and perhaps new uses for peanuts and peanut proteins. Peanut constituents and their modification by processing that influence nutritive properties and consumer acceptance of processed peanut product are also studied. The Crops Research Division of ARS and several State Experiment Stations, including Georgia, Alabama, and Texas, cooperate in the research by providing samples of peanuts of known variety and of known growing, harvesting, and drying histories. Louisiana State University cooperates by conducting evaluation tests on selected peanut isolates. Research on new and improved food products, and new and improved processing technology for peanuts are conducted at New Orleans, Louisiana. In the food products work, emphasis is on obtaining a stable, defatted whole peanut (kernel) product of long shelf life, which also meets the requirements of taste, odor, color, texture, and appearance. Several industrial concerns specializing in peanut products cooperate by supplying deskinners and by evaluating the experimental products. The processing research consists of investigations of procedures for large scale production of defatted whole peanuts. Industrial concerns are cooperating in the determination of the necessary processing conditions for such operations as desolventization and roasting.

The Federal scientific research effort in this area totals 5.1 professional man-years. Of this number 4.1 is devoted to chemical composition and physical properties, 0.5 to new and improved food products, and 0.5 to new and improved processing technology.

The following line of work was terminated during the year: (1) Investigations to isolate, identify and measure chemical constituents in peanuts which contribute to quality of processed peanut products (under chemical composition and physical properties).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 2.2 professional man-years effort, divided among subheadings as follows: chemical composition and physical properties, 0.7; new and improved food products, 1.2; and new and improved processing technology, 0.3.

One State Experiment Station is investigating chemical composition and physical properties of peanuts as these relate to susceptibility of various strains of Spanish peanuts to rancidity development. Determination of phosphorus content, level of free fatty acids and susceptibility of oils to autoxidation has been made for peanuts of known genetic history and maturity in a search for means of control at the genetic level. A second program includes a comprehensive investigation of the chemical composition of peanuts as composition is affected by environmental and agronomic factors. Flavor of peanuts is also being determined in an effort to note any effects due to production practices or handling.

Two main phases of work are underway on new and improved peanut food products. One phase is directed toward development of more dependable and efficient methods of curing peanuts which will yield peanut products of high quality and free of bitterness; the second seeks to determine the effect of various treatments (temperature, time, moisture and storage conditions) upon the keeping qualities of peanuts and peanut products in common and refrigerated storage. In the latter study, the influence of variety, grade and prestorage quality of peanuts on processing characteristics and on shelf-life of peanut products is also obtained.

Aroma and flavor characteristics of peanuts are developed from the basic constituents of raw peanuts by reaction at roasting temperatures. One station is conducting research on improved processing technology for peanuts by investigating the chemistry of the process of roasting peanuts and the effect of variations in roasting on the resulting product. It is expected that characterization of the substances responsible for the aroma and flavor of roasted peanuts will lead to identification of the precursors of flavor and aroma to be found in raw peanuts.

Industry and other organizations also conduct research of interest and value in this area. The estimated annual expenditures are equivalent to approximately 8 professional man-years. Of this total, about 6 man-years is by processors and 2 man-years by equipment manufacturers. For the most part food processors are engaged in improving peanut butter and peanut-containing confections. Research is directed toward improvements in the texture, appearance, and mouthing properties of peanut butter and in the stability, appearance, texture and flavor of roasted or salted peanuts and of peanut-containing products. A limited amount of attention is being given to processing peanut oil for edible purposes and to peanut flour as a food constituent. There is limited effort on the part of the industry to develop fundamental information on peanuts either as a food item or as a potential raw material for industrial use. Frequently such information is sought from the Southern

Utilization Research and Development Division by representatives of the industry. Information concerning problems of the peanut industry is exchanged through representatives of the National Peanut Council and of the industry at meetings of the Peanut Improvement Working Group. Some attention is given by equipment manufacturers to improving equipment for shelling and grading peanuts with respect to size and color, and for blanching and roasting.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Structural Factors, Properties, and Reactions of the Proteins. Pioneering research in scientific fields involving seed proteins and associated substances was continued as a basis for development of new concepts and possibly new uses for these materials. Major areas of recent research have included studies of seed globulins, of their subcellular distribution, and of a specific group of seed proteins, the lipases.

Research on isolation and chemistry of seed globulins has shown that ultracentrifugation is sensitive to protein interaction and, therefore, is a relatively unreliable method for analyzing seed proteins. It has been found possible, however, to apply chromatography on DEAE cellulose and the new technique of zone-electrophoresis on Cyanogum gel to the total proteins of the peanut. In both these instances these methods are much less subject to protein interaction and may be relied upon to reflect accurately the composition of mixtures and the progress of fractionation. With the aid of these two tools and by scaling up the process of chromatography, it has been possible to isolate a pure globulin from peanuts which has been named α -conarachin, and which is now being studied extensively for structure and composition. This globulin disappears from the peanut in the first few days of germination as shown by chromatography, and it is very sensitive to the environment - by simply changing ionic strength and pH molecular weights varying from 145,000 to 500,000 are obtained. In the presence of low concentrations of sodium dodecyl sulphate or concentrated urea, particles of molecular weights of less than 10,000 can be noted. This leads to the belief that the major primary unit is of low molecular weight, and that perhaps several types of primary units go in to make the final major structure.

One of the classical seed proteins, edestin from hempseed, has now been shown to be a mixture by cellulose chromatography at elevated temperatures. This procedure opens the way for chromatography of insoluble proteins without resorting to extremes of pH. This procedure is being employed to isolate pure proteins from hempseed.

Two independent methods have been developed for subcellular fractionation of the contents of the peanut parenchyma cell. The first method which involves fractionation in the absence of water has resulted in obtaining protein rich particles with protein concentrations up to 85%. These particles do not exhibit any enzymatic activity. However, protease activity has been found in the cell wall fraction, and hexokinase activity in a fines fraction. A second fractionation using concentrated sucrose and Carbowax solutions has demonstrated that about 75% of the protein of the peanuts are in subcellular particles, and are not released into solution in the presence of the aforementioned osmotic agents. Among these proteins is α -conarachin. A new

approach has therefore been made available for studying the biological function of the major seed globulins which have been shown to be in subcellular particles - by isolating and studying the biochemistry of the particles themselves.

In the course of these studies, unique distributions of components have been found. For example, all of the phytic acid is found in a protein rich component (aleurone grains), as well as the greater proportion of magnesium and potassium. The major proportion of calcium is found in the cell walls and the major amount of sucrose and nucleic acids in the fines fraction (reticulum).

The mobilization of fat in oilseeds takes place rapidly in the early days of germination and is one of the important physiological processes for mobilization of energy to support the growth processes. The first step in the mobilization is lipolysis of the glyceride, or otherwise making available the acyl group for further metabolism. The proteins involved in this process have been investigated in two lines of research: (1) the study of lipolysis in resting seeds as observed in the castor bean; (2) study of the development of lipolytic systems in germinating seed. For the purpose of comparison, the castor bean was chosen for this study as well.

The study of the lipase in castor beans has resulted in the isolation of a particulate preparation which contains the acid lipase free of all substrate, and of most of the other proteins. This preparation is very active and quite stable. There seems to be evidence of two enzymes in this preparation: one with a maximum activity for triglycerides of C_6 saturated fatty acids and the other with maximum activity for glycerides of long-chain unsaturated fatty acids. One of the problems in understanding the catalysis of heterogeneous reactions involving water and insoluble material such as fat, is to find the means of bridging between the two in the catalytic action. Accordingly, one phase of the research has sought the removal of a factor from the enzyme which might perform this function. Success has been achieved in removing from the acid lipase a lipid material which acts as a cofactor for hydrolysis of triglycerides of long-chain fatty acids. This is the first time that a cofactor for a lipase has been reported. And this work has taken an exciting turn with the finding that α -tocopherol succinate can substitute for this lipid cofactor. This is the first time that an enzymatic role for tocopherols has been found.

The lipase of the resting castor bean is more typical of lipolysis in animal or plant adipose tissue than is the lipase of the gastrointestinal tract. Information on the properties of the castor bean lipase will therefore have general meaning, not only for plant tissue lipases, but possibly also for animal lipases. The fact that tocopherol is involved in lipase activity might even suggest a role for tocopherol in a field so far away from the original purpose of investigation as atherosclerosis.

The methods used to study the fatty acid content of serum lipids have been applied to the germinating castor bean. It has been shown that there is a sharp increase in fatty acid content up to four days of germination, following which the fatty acid content decreases sharply. This will be the basis for selection of ideal conditions for isolation of the lipase in the germinating seed.

2. Identification of Factors Influencing Flavor, Aroma, Color, Structure, and Nutritive Value of Processed Products. In contract research at the University of Arizona, which is now terminated, investigations were continued to study the influence of processing on the composition and flavor of peanut products. The concentrations of free arginine, histidine, aspartic acid, lysine, proline, serine and threonine were determined through the use of ion exchange methods for the roasted fat-free peanut flours for the 1957 and for the 1958 crops of the varieties Argentine, Florispan Runner, Fla. 302-12-B-28, Tennessee Red and Dixie Runner. Arginine, histidine and lysine determinations were made on two varieties of peanuts from the 1957 crop and on the five varieties of the 1958 crop in the "uncured, dried and refrigerated" treatment. The free alanine, aspartic acid, glutamic acid, glycine, proline, serine, cystine, threonine and valine were determined on the flour obtained from "uncured, dried and refrigerated," and for the "cured, refrigerated" for the 1957 and 1958 crops. Non-protein, total and amino nitrogen, total sugar, and oil contents were also determined for all treatments for the five varieties.

The data for the free amino acids in the peanuts as determined by ion exchange methods and by microbiological methods were not in agreement. This points to the fact that microbiological methods may not be relied upon in the determination of free amino acids in plant extracts. Evidence for the reduction of the amino nitrogen in peanut proteins on the roasting of peanuts suggests that lysine may be affected by the roasting process. No clear cut pattern of a relationship between the free amino acids in peanuts and the quality factors such as aroma, flavor, color and texture evolved from the studies. The wide variation in the intensity of the quality factors observed in the samples studied indicate that sampling of peanuts over wide geographical areas and growing conditions is essential for quality comparisons of varieties and for the ultimate correlation of quality factors and constituents of raw peanuts.

As an aid to better understanding and assessing the quality factors of processed peanut products, further in-house research was conducted on the isolation and characterization of chemical constituents in peanuts which might affect nutritive properties and consumer acceptance. The myotonic factor in peanuts has been concentrated 15,000-fold. Its physiological activity is lost on mild acid or alkaline hydrolysis. This material has been shown by paper chromatography to consist of two major components and at least one minor one. One of the crystalline materials isolated in the course of fractionation of the alcohol extract of de-oiled peanuts was identified as pinitol, a monomethyl ether of D-inositol. Investigations will be continued to identify the hemostatic factor and other crystalline products in the alcohol extract. The physiological tests on various peanut fractions are carried out in the Department of Zoology at Louisiana State University. (S4 1-87, S4 1-100).

B. New and Improved Food Products

1. Defatted Whole Peanuts. Research to develop defatted whole peanuts (kernels) as a new confection was conducted. Interest in defatted peanuts is due to several factors, including lower caloric value, possible increase in shelf-life by minimizing oil rancidity, possible use by hemophiliacs to control bleeding, and opportunity for increased utilization of peanuts.

Roasted Virginia peanuts were solvent extracted with hexane to different levels of oil removal, and then desolventized. Some of the samples of defatted desolventized peanuts were salted, either by dipping in saturated salt solution at room temperature or preferably by dipping in water and sprinkling with salt. The wet peanuts were oven dried. The most acceptable product (salted or unsalted) proved to be the defatted peanuts with 81% oil removed. The peanuts have a good appearance, and their taste is considered acceptable even though it is not like that of the original roasted peanuts. Packaging of the product in metal cans, in either vacuum or in an atmosphere of nitrogen containing less than 2% oxygen, maintained the peanuts in good condition even after one year storage time. In cellophane-type packages, defatted peanuts tended to pick up excessive moisture within 30 days. Other types of flexible packaging are being investigated.

C. New and Improved Processing Technology

1. Processing Technology Related to Defatted Peanuts. Based on earlier laboratory experiments in producing defatted peanuts, pilot-plant runs were conducted to prepare large amounts of materials for taste and appearance evaluation, to obtain pilot-plant processing data for cost calculations, and to investigate practical methods of desolventization of the extracted peanuts and other processing steps. Fully roasted and one-half roasted Virginia peanuts were batch extracted with hexane for 23, 47, 71, 120, and 335 hours at room temperature to remove 38, 61, 71, 81, and 92% oil, respectively. The fully roasted peanuts with 81% of the oil removed have the best appearance. Low rates of extraction indicate that a batch method would be required for large scale processing.

The extracted, solvent-wet peanuts were desolventized by (1) air drying followed by drying in a forced draft oven at 150° F. and then at 212° F., (2) direct drying in a forced draft or vacuum oven at a low initial temperature of 150-167° F. followed by 212° F., or (3) direct drying in a forced draft or vacuum oven at 212° F. Drying at a lower initial temperature appears to give a better tasting defatted peanut especially when a forced draft oven is used. A minimum total drying time of 9 hours is required to remove the last traces of solvent.

A preliminary cost study for defatting Virginia peanuts with hexane in three all-new hypothetical commercial plants indicates operating cost can be as low as 74 cents for a volume equivalent to the 14 oz. pack popularly merchandized in 503 x 308 tins. Using fully depreciated equipment reduces operating cost of the equivalent of the 14 oz. pack to 61.5 cents.

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AREA NO. 8 - TUNG PROCESSING AND PRODUCTS

Problem. Tung oil has lost much of its traditional market in protective coatings to synthetic raw materials. New and improved industrial products from tung oil must be developed to recapture lost markets, maintain present markets, and provide new outlets for surplus tung oil. Basic information is needed on the chemical composition and properties of tung oil and its fatty acids, and on the chemical modification of these materials to permit more effective exploitation of their unique characteristics in protective coatings, agricultural and industrial chemicals, surfactants, and plasticizers. For example, improved coatings utilizing tung oil are needed to meet increased performance demands and competition from synthetic polymeric coatings. Intumescent fire-retardant coatings and water-reducible coatings containing tung oil are desired. A limited market of low economic value exists for tung meal as a fertilizer. Research is needed to develop more information on the profitable industrial uses for tung meal and its protein to the benefit of the overall economy of the tung industry.

USDA PROGRAM

The Department has a continuing long-term program involving organic chemists engaged in both basic and applied research on tung and its products. Emphasis in the present program is on development of new and improved industrial products from tung oil and its derivatives.

Research is conducted at New Orleans, Louisiana to develop fundamental information on the chemical composition, properties, structural factors and reactions of oilseed proteins, as a basis for development of new concepts and possibly new uses for oilseed proteins, including tung protein. Research to develop new and improved industrial products from tung oil is carried out at New Orleans, Louisiana, with cooperation and support by the Pan American Tung Research and Development League, the U. S. Army Engineers Research and Development Laboratories and the U. S. Air Force. The league maintains a part-time Fellow at the Southern Regional Research Laboratory for research on the production of improved protective coatings from tung oil. The major emphasis is placed on the development of exterior, intumescent fire-retardant surface coatings using tung oil alkyds. The tung alkyds are being chemically altered and formulations modified to produce coatings which will intumesce to give a thick cellular, fire-resistant material upon thermal or flame exposure. The U. S. Army Engineers Research and Development Laboratories evaluate the more promising fire-retardant coating formulations developed with their support. Other investigations involve studies of the chemical modification of tung oil and its fatty acids to produce chemical intermediates having utility in protective coatings, and as agricultural chemicals, surfactants or plasticizers. Informal cooperation is maintained with industrial firms and other agencies for the evaluation of promising chemical intermediates for specific end uses.

The Federal scientific research effort in this area totals 4.8 professional man-years. Of this total 0.6 is devoted to chemical composition and physical properties, and 4.2 to new and improved industrial products.

The following line of work was terminated during the year: (1) Applications research on vehicles and surface coatings containing derivatives of tung oil (under new and improved industrial products).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 did not report any effort in this area of research.

Industry and other organizations conduct limited research in this area, the estimated annual expenditures in the United States being equivalent to approximately 9 professional man-years. Of this total about 4 man-years' effort is by the Pan American Tung Research and Development League, 3 man-years by the protective coatings industry, and 2 man-years by chemical concerns.

Research to develop new or improved products from tung oil is being supported cooperatively by tung growers and processors in the United States and Argentina at their Pan American Tung Research and Development League Laboratory at Picayune, Mississippi, and elsewhere by contracts. Under development are water-thinnable tung oil paints for the automotive industry, products from oxidized tung oil, and plastics. The League supports a part-time Fellow at the Southern Utilization Research and Development Division and there is frequent exchange of information on research developments.

Although over 80% of tung oil consumption is in the protective coatings industry, this industry's research effort on tung oil is quite limited since it has no vested interest in tung oil and there are many competing raw materials from which to choose. Several producers of emulsion-type paints or polymers for such paints are evaluating emulsifiable tung oil as an additive to improve adhesion in repainting chalky surfaces.

One large chemical concern is conducting research to develop uses for their recently introduced product, an acrolein adduct of tung oil. Exploratory work on this type adduct was carried out at the Southern Division. Several companies have been furnished samples of tung monoglycerides prepared at the Division for evaluation as an emulsifier-sticking agent for insecticides and one company has produced tung monoglycerides on a laboratory scale.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Structural Factors, Properties and Reactions of the Protein. The composition, properties, structural factors and reactions of oilseed proteins and associated materials are being investigated as a basis for development of new concepts and possibly new uses for oilseed proteins, including tung protein. Major areas of recent research have included studies of seed globulins, of their subcellular distribution, and of a specific group of seed proteins, the lipases. Since peanuts were found to be an especially suitable experimental material and employed for much of the fundamental research on seed proteins, the report of progress in the research is given in Area No. 7, "Peanuts Processing and Products."

B. New and Improved Industrial Products

1. Exterior Intumescent Fire-Retardant Surface Coatings from Tung Oil Alkyds. More than 11,000 lives are lost annually in the United States by fire, and our property losses by fire amount to over one billion dollars a year. Effective fire-retardant protective coatings could greatly reduce this loss of life and property.

Research supported in part by the U. S. Army Engineers Research and Development Laboratories and the U. S. Air Force, and assisted by a part-time Fellow of the Pan American Tung Research and Development League, has been continued to develop exterior, intumescent fire-retardant protective coatings from tung oil alkyds. The fire-retardant paints previously prepared from tung oil alkyds and various types of gas-producing components have been modified to improve their thermoplastic, fire-resistant and intumescent properties. Improvements were achieved by lowering the pigment-vehicle ratio, by modification of the binder, and by incorporating better gas-producing and fire-resistant components in the undercoat. However, these multiple formulation, two- or three-coat paint systems (gas-producing undercoat, covered with a resistant topcoat) still lacked the desired foam-forming, carbon-forming and fire-resistant properties.

In more recent work, encouraging progress was made in preparing intumescent fire-retardant films using single formulation, two- or three-coat, foam-forming paint systems. This was achieved by incorporating water-insoluble or relatively water-insoluble organophosphorus, organohalophosphorus, organonitrogen and polyhydroxy and polyurethane derivatives into the formulations. Previously, it was impossible to prepare intumescent fire-retardant paint films with a single formulation system. A resistant topcoat formulation was always necessary to trap some of the evolved gas. The new foam-forming formulations produce coatings exhibiting remarkable water resistance. In some cases the water resistance is actually improved by exposure to water. Preliminary tests indicate that films of these paint also have good thermal shock resistance and recoatability. When evaluated in USAERDL's fire-test cabinet (a relatively mild test), many of the paint formulations exhibited good intumescent fire-retardancy. However, when the best formulations were tested in the more severe Forest Products Laboratory's 8-foot tunnel furnace, only limited fire-retardancy was obtained. This pointed to the necessity of developing a more rigorous laboratory fire-retardancy screening test than the conventional fire-test cabinet method. A simple, yet severe screening test has been developed at the Southern Regional Research Laboratory. Using the test as a guide, improved fire-retardant coatings have been made. One recent formulation exhibited fairly good fire-retardancy when tested in the 8-foot tunnel furnace. Further improvements in spumific (foam-forming) and carbonific (carbon-forming) fire-retardancy action, can stability, brushability, drying characteristics, color and tint retention, water resistance, mildew resistance, and weatherability will be sought. (S4 1-98)

2. Chemical Modification of Tung Oil to Produce New and Improved Products Such as Protective Coatings, Agricultural Chemicals, Surfactants and Plasticizers. Tung oil and tung methyl esters adducted with acrylic acid were formulated into water dispersible alkyds by cooking with polyethylene glycol, a triol, and phthalic anhydride. The aqueous dispersions at 33% solids content were stable on aging and to freeze-thaw cycles. With melamine resin,

they formed films which could be baked to give coatings having good hardness, adhesion and flexibility, and resistant to water, salt water, detergent, mineral spirits, and gasoline. The formulations have good possibilities for use as primers but are not sufficiently resistant to ultraviolet light for use as finish coatings.

Evaluation of tung oil-zinc resinate-pentalyn G varnish vehicles, in which one-third or one-half of the zinc resinate was replaced with lead resinate, showed that the drying times were appreciably reduced. The promising new formulations are comparable to standard modified phenolic resin varnishes and fast drying alkyd resins.

Under contract work (now terminated) at the University of Florida concerned with applications research on vehicles and surface coatings containing derivatives of tung oil, tung monoglycerides in combination with ammonium eleostearate or ammonium oleate were evaluated as dispersing agents for pigments in typical resin emulsion paints. Tung monoglycerides and ammonium oleate, in combination with commercial dispersing agent Tamol 731 in an acrylic type resin emulsion, gave a coating with somewhat better water resistance than that produced with commercial dispersing agents. (S4 1-78(C)).

Limited research has been carried out under a new project whose objective is to chemically modify tung oil and its fatty acids to produce materials having utility as agricultural chemicals, surfactants or plasticizers, and in protective coatings. Preliminary experiments indicate that it may be possible to obtain a paint oil of improved water resistance and brushing characteristics by heat processing tung and soybean oil at low temperature in the presence of a catalyst. This will require confirmation. It is planned to direct the research initially toward development of an air drying, water reducible tung oil vehicle as a protective coating. The Pan American Tung Research and Development League supplies a part-time Fellow who gives advice and assistance in the production of improved protective coatings. (S4 1-93).

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AREA NO. 9 - CITRUS AND SUBTROPICAL FRUITS PROCESSING
AND PRODUCTS - SOUTHERN LABORATORY

Problem. The citrus and subtropical fruit production of the Southern Region is an expanding industry with the need for the development of better, as well as new-type consumer products, and for the improvement of present or invention of new processing procedures and machinery. These advances are required to regularly utilize the currently large production, particularly of oranges and grapefruit, and the anticipated higher production of these fruits, to the economic advantage of the growers and consumers. Basic research is needed to lay the groundwork for these advances. This research is needed, for example, on the composition and physical nature of essential oils, flavonoids, including bitter constituents, constituents responsible for oxidized off-flavors, carotenoids, and the like, which determine many of the sensory characteristics, and which affect product quality and stability. Other problems whose solutions are dependent upon the availability of more detailed compositional and physical data are: cloud stability, gelation, discoloration, fermentation, and the like. Increased production of citrus has stimulated the development of new products but many of these are urgently in need of improvement which will depend in part upon advances in basic research. New products are needed to attract new markets and also to reduce packaging and shipping costs. Research is needed to improve frozen citrus concentrates as processing procedures change, to develop better high density concentrate products, citrus powders, chilled juice and section products, pulp-fortified products, and to develop new or improved canned products which have a natural fruit flavor. Along with progress on product development there is a serious need to improve the actual processing procedures, processing equipment, and packaging operations and materials, to obtain and maintain the most desirable fruit characteristics. As an illustration, research is needed to develop less expensive dehydration equipment and an improved process for the production of citrus powders.

USDA PROGRAM

The Department has a continuing long-term program involving biochemists, organic chemists, bacteriologists, food technologists, and a chemical engineer engaged in both basic and applied utilization research studies on citrus and subtropical fruits of the Southern Region to develop new or extended uses for these commodities.

Research to develop basic information on chemical composition and physical properties of citrus and subtropical fruits, and their products and byproducts is conducted at the U. S. Fruit and Vegetable Products Laboratories at Weslaco, Texas and Winter Haven, Florida. This information provides the necessary basis for efficient research in developing new and improved food products and processing technology. At the Weslaco Laboratory the program includes investigations of the origin of carotenoid precursors and the biochemical mechanisms of their conversion to carotenoids in grapefruit as a basis for improvement of processing characteristics of and products from colored grapefruit. The Texas Agricultural Experiment Station (substation 15, Weslaco), Citrus Rootstock Investigations Laboratory (CR,ARS, Weslaco), and the Texas College of Arts and Industries are providing grapefruit of known history and conducting, or cooperating in conducting, on the tree tests. At the Winter Haven Laboratory the program

includes investigations of the neutral fraction of orange peel extract with the aim of isolating, characterizing, and identifying those substances, particularly bitter principles, that are most detrimental to the flavor of orange products. Investigations are also in progress on the composition of essential citrus oils as related to flavor of juices, concentrates, powdered juice, and other products; and on investigations of the chemical and physical nature of components of cloud of orange juice to provide better understanding and control of factors affecting stability of orange juice products. Close consultation is maintained with the Florida Agricultural Experiment Station (Citrus Experiment Station, Lake Alfred) and the industry.

Research to develop new and improved food products is carried out at the U. S. Fruit and Vegetable Products Laboratories at Weslaco, Texas, and Winter Haven, Florida. At the Weslaco Laboratory the major applied effort is to develop products which will make greater and more efficient use of grapefruit, as for example, pulp-fortified frozen grapefruit concentrates and grapefruit drinks. This research is being carried out in part in cooperation with several state and private organizations. The cooperators provide fruit or raw materials, such as pulp and juice, of known history. Processing plant facilities are available from the Texsun Citrus Corporation (Weslaco) and Rio-Vac, Inc. (Harlingen). Other research includes investigations to develop new and improved processed products from selected minor fruits, such as avocados, usually in cooperation with, and originating in requests from the State Experiment Station and industry associations. Formal agreements exist with the Texas Agricultural Experiment Station (College Station and Weslaco), with Texsun Citrus Corporation (Weslaco) and with Rio Farms, Inc. (Edcouch). Informal cooperation is maintained with Texas Citrus Mutual, Inc. (Weslaco), Texas Cannery Association (Weslaco) and such other organizations as are found necessary for the procurement and processing of fruit. Research is also underway in the U. S. Fruit and Vegetable Products Laboratory, Winter Haven, Florida, on the improvement of chilled citrus products. Cooperation is informal with industry.

In the field of new and improved processing technology, research is being carried out at the U. S. Fruit and Vegetable Products Laboratory, Winter Haven, Florida, to determine how the "foam-mat" type of air-drying can be applied for the preparation of dried citrus products of optimum flavor and stability. This research is being conducted in cooperation with the Western Utilization Research and Development Division (ARS) and the Florida Citrus Commission under a formal memorandum of understanding.

The Federal scientific effort at the Southern Division devoted to research in this area totals 17.9 professional man-years. Of this total 7.5 is devoted to chemical composition and physical properties, 6.7 to new and improved food products, and 3.7 to new and improved processing technology.

The following line of work was terminated during the year: (1) Studies on the chemistry and the mechanism of formation of oxidized flavors in citrus products (under chemical composition and physical properties).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

Related programs of all State Experiment Stations and Industry and other organizations are reported by the Western Utilization Research and Development Division in Summary of Current Program and Preliminary Report of Progress.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Chemical and Physical Properties of Flavoring Constituents of Florida Citrus and Subtropical Fruit Products. Research has been conducted to determine the factors responsible for the formation of oxidized flavors and the chemistry involved, with a view to possibly preventing such off-flavors in commercially produced citrus products. "Citrus oxidized flavor" (COF) also referred to as "cardboard off-flavor" and "castor oil flavor" is not known in freshly prepared citrus products but arises during frozen storage and disappears on further storage. Positive tests for aldehydes were obtained in the volatile materials from off-flavored (COF) concentrate. The odor of off-flavored concentrate was reproduced by the addition to a good flavored concentrate of 1 part per million or less of saturated aliphatic aldehydes of 8 to 10 carbon atoms. This simulated off-flavor disappeared in storage in a manner analogous to the naturally occurring off-flavor.

Improved extraction and recovery methods have shown that total recoverable carbonyl compounds decrease in orange juice and concentrate during storage at the same time that the flavor typical of the freshly prepared product decreases, suggesting that flavor changes may be due in part to loss in carbonyls. At least 6 carbonyls were detected in the extracts. Five of these have been identified as n-heptanal, n-octanal, n-nonanal, n-decanal, and n-undecanal. (S3 2-28).

A new research approach to the study of flavoring constituents and the chemistry of off-flavors of citrus products was recently initiated. The research involves investigations on composition of essential citrus oil as related to flavor of juices, concentrates, powdered juice, and other products, with special emphasis on essential orange oil. The principal flavoring components of orange products are found in the essential oils. In initial research, numerous terpene and carbonyl compounds were separated from essential orange oil and identified. The components identified were: alpha-pinene, camphene, sabinene, myrcene, alpha-phellandrene, alpha-terpinene, d-limonene, gamma-terpinene, p-cymene, terpinoline, carvone, undecanal, dodecanal, n-octanal, n-nonanal, n-decanal, citronellal, geranial, neral, and alpha-terpineol. Commercial orange oil has been separated into terpene fractions in macro quantities (6 pounds) using silicic acid for the purpose of obtaining sufficient material of the four terpenes remaining to be identified. Good progress has been made in characterizing these terpenes. Following the completion of identification of various constituents, the results and techniques will be used to study chemical changes orange oil undergoes under various conditions of storage, handling and processing. (S3 2-36).

2. Investigation of Bitter Principles and Flavonoids in Florida Citrus Products. Undesirable peel substances, including bitter principles, probably cannot be entirely excluded from mechanically extracted orange juices. Nevertheless, identification of these substances could be an important step in effectively limiting the amounts, especially if they could be quantitatively determined. Such methods should be of considerable value in controlling orange juice product quality.

In continued work on a bitter benzene extract of orange peel juice, six crude fractions of differing characteristics were separated. From the largest of these, which was neutral in reaction, a flavone believed to be new was isolated. Subsequent work on its structure showed it to be 3',4',5,6,7-pentamethoxyflavone. Although this compound appears to be about as bitter as naringin when dissolved in alcohol and diluted with water, its concentration in the peel juice is quite low. However, it undoubtedly contributes to the overall taste. The concentration in the peel juice was about 1 gram in 25 liters; while a good grade of grapefruit juice might contain five to ten times that amount of naringin. Added to water in the proportion in which it was isolated, the flavone could not be detected by a taste panel. At twice the concentration its presence was apparent. (S3 2-30).

Recently, a chromatographic system using Supercel columns has been developed which is capable of partially separating the neutral fraction of a benzene extract of orange peel juice into its components. The five distinct portions separated have been tentatively identified as linalool plus terpineol (odor), tangeretin, nobiletin, heptamethoxyflavone, and the pentamethoxyflavone described above. Refinements in the system will be sought.

A midseason peel juice has been found that is not markedly bitter, suggesting the desirability of monitoring peel juice bitterness throughout a season. If a monthly check of peel juices planned for next season shows that bitterness occurs only part of the time, this could furnish valuable information to the industry in adjusting their extractor pressures for optimum quality of juice. (S3 2-37).

Another phase of work has shown that sludge from the winterizing of tangerine peel oil is an excellent source of tangeretin. About 4 gallons of the sludge yielded a little over 2 gallons of oil and 2104 grams of tangeretin. The process involved filtering off the oil and washing the solids with petroleum ether. The solids were then recrystallized from ethanol, washed with aqueous alkali, and again recrystallized from ethanol. (S3 2-30).

3. Factors Affecting Physical Characteristics of Processed Citrus Products.

A stable cloud is considered to be an essential characteristic of high quality orange juice products. Initial research on the chemical and physical nature of components of cloud to provide better understanding and control of factors affecting stability of orange juice products, has been principally devoted to development of methods of preparation and analysis of cloud. Essential oils and lipids are less abundant, and nitrogenous materials more abundant, than was suspected. Remarkable stability of cloud was obtained by extensive reduction of soluble solids by dialysis.

Effort will be directed toward developing more accurate procedures for determining gross composition of the various fractions of cloud, particularly the cellulosic and nitrogenous components. Surveys of the effects on cloud composition of variety, methods of juice extraction, etc. will follow. (S3 2-38).

4. Basic Investigations of Carotenoids in Grapefruit. A thorough knowledge of carotenoid formation in colored grapefruit should provide information useful in improving processing characteristics of, and products from, colored grapefruit. It should also be helpful in developing more highly colored fruit and in retention of color in fruit developed for processing purposes.

Cooperative work with the California Institute of Technology on the biochemical pathways of pigment formation has been terminated. In the joint investigations tomatoes were used instead of grapefruit because of their more rapid rate of metabolism of the carotenoid pigments. Labelled compounds (radioactive) were used in the investigations. Glucose was demonstrated as a carbon source for the carotenes. Acetate is apparently incorporated via mevalonic acid. Glucose is a more efficient precursor of carotenes than acetate though less efficient than mevalonic acid, but only small amounts are incorporated into the unknown colorless compounds. Carbon dioxide is incorporated at about the same ratio as glucose. Glucose and carbon dioxide appear to be incorporated through a 20-carbon precursor (3,7,11,15-tetramethylhexadeca-1,3,6,10,14-pentaene).

The development of chromoplasts in Ruby Red grapefruit has been studied. It was found that shortly after degradation of the chloroplasts, lightly colored birefringent droplets were formed. The droplets increased in color and birefringence and finally assumed a definite shape. While lycopene was the most abundant pigment and was increasing, the chromoplasts appeared as red needles as in tomato fruit. As the lycopene content of the grapefruit decreased and β -carotene content increased, pink platelets were found. They were similar in shape to carrot chromoplasts but different in color. A similar study with white grapefruit indicated that chromoplasts did not form, but even late in development transparent spheres similar in size and shape to chloroplasts could be found. It is considered possible that chloroplasts of low carotenoid grapefruit do not fragment as readily as in colored varieties.

Immediately following the January 9-12, 1962 freeze in the Rio Grande Valley, Texas, cooperative work was undertaken with Crops Research Division, ARS, personnel on the development of a test for freeze damage to citrus trees. The test consists of cutting a 6 mm. plug of bark from a branch to be tested and incubating in 0.5% aqueous tetrazolium red for one hour and noting the color change. It is capable of distinguishing islands of living cells among dead cells and may be useful in basic studies on freeze damage. It cannot predict whether the living cells that have been exposed to freezing temperature will die.

Several other miscellaneous studies were undertaken during the 1961 and 1962 seasons that did not lead to conclusive results but did indicate interesting leads for research. Five of these involved incorporation of labelled carbon dioxide into grapefruit on the tree; attempts to develop a cell-free system for the study of the synthesis of carotenes; pigment analysis of fruit from nucellar red grapefruit trees (cooperative with CR,ARS); effect of artificial cooling of tree on pigment formation in fruit; and investigation of the seasonal changes of lycopene in off-bloom fruit. With respect to the last item, the results indicating that the age of fruit is more important than season of the year in regulating lycopene content of red grapefruit may show that internal factors are more important than external factors in influencing lycopene accumulation or depletion. (S3 2-34).

B. New and Improved Food Products

1. Improved Chilled and Canned Citrus Products. Investigations were completed on the microbiological spoilage of chilled citrus salads. At temperatures above 40°F. the shelf life of the unpasteurized, chilled products, as judged

by organoleptically detected spoilage, was too short to permit widespread marketing. Spoilage occurred in 5 to 6 weeks at 40°F. and was little influenced by low levels of benzoate or sorbate as preservatives. At 30°F. the products have a good shelf life which was increased from 12 weeks for the controls to 16 weeks by as little as 0.033% preservative in the cover syrup. Shelf life was not correlated with increase in microbial populations since spoilage was observed at 30°F. with populations below 100,000 per ml. of cover syrup. At 50°F. plate counts were well over 1,000,000 per ml. before spoilage was detected. Initial plate counts averaged 15,000 per ml. Preservatives were more effective at maintaining low microbial populations than in extending shelf life of citrus salads at the higher temperatures. Evidence was found for the loss early in the storage period of a characteristic fresh citrus flavor. This flavor change was not associated with incipient spoilage. Demonstration that chilled citrus salad products may be kept in acceptable condition for longer periods than are now common in commercial practice, by careful control of temperature and selective use of chemical preservatives, should encourage the improvement of processing and handling conditions with ultimate lowering of costs and increased consumer use.

Factors affecting microbial spoilage, retention of fresh flavor and physical stability of chilled citrus juices are being studied as a basis for developing improved processing practices and improved products with a longer shelf life and a wider distribution potential.

In further experiments to determine the growth rates of pure cultures of known spoilage organisms in the presence of preservatives, addition of even low levels (0.033%) of potassium sorbate to a simulated cover syrup had a noticeable inhibitory effect on both yeasts and bacteria, being considerably more effective against the former. The preservative was significantly more inhibitory at low pH (3.5) within the normal range for citrus salads. Dehydroacetic acid alone or in combination with benzoate or sorbate was more lethal against the organisms than was benzoate or sorbate alone.

In other experiments various preservatives (.033% sodium benzoate, 0.33% of a 2:1 mixture of the methyl and propyl esters of p-hydroxybenzoic acid, and .033% benzoate and .033% ester mixture) were used with or without heat treatment in the 120° to 160°F. range. The addition of preservatives to unheated juice reduced microbial counts. Unheated samples were found to be off-flavor in about 3 weeks; the heated samples in 3 to 5 weeks. Heat treatments to 160° in the presence of preservatives were not more effective than heat treatments without preservatives. Ascorbic acid values decreased during storage (40°F.) to about half the initial value.

Endeavors in other experiments to lengthen the storage life of chilled orange juice with Vitamin K₅ alone or in combination with various anti-oxidants were not successful in the sense that ascorbic acid (Vitamin C) decreases rapidly in proportion to the concentration of Vitamin K₅.

In experiments in progress, variables such as temperature and time of heating, temperature of storage, with and without preservatives, and time of harvest and processing of fruit for juice, are being investigated to determine their respective effects on shelf life and characteristics of chilled orange juice. Preliminary data indicate shelf life is influenced more by temperature of storage than by heat treatment or addition of preservatives. Off-flavors may develop in spite of lack of bacterial growth. (S3 2-35).

2. Improved Frozen Concentrate Citrus Products. Investigations to determine the effect of adverse storage (exposure to temperatures above 0°F.) on the residual storage life of frozen concentrated citrus juices have been completed. In the research, frozen concentrated citrus juices (25 lots of orange, 1 of grapefruit and 1 of tangerine) were collected from commercial processors, 1957-60 seasons inclusive, and tested for stability at 40°F. (household refrigerator temperature) before and after storage at selected temperatures. Sub-lots of each were held at temperatures of 20°, 15°, 10°, 5° and 0°F. for various combinations of times and temperatures sufficiently mild that the concentrates would not show losses of cloud or flavor upon immediate reconstitution.

Cloud stability in concentrates as received varied from 4 to more than 340 days at 40°F., and this characteristic stability was not materially affected by extended storage at 0°F. Exposures to temperatures above zero resulted in reduced cloud stability, and the effects of separate periods of such adverse storage were additive. Concentrates produced after a major freeze, in the 1958 season, possessed cloud stability comparable to that of other concentrates. Those produced in the 1957 season exhibited flavor stability equal to or greater than their cloud stability, but the cloud stability of the 1960 concentrates greatly exceeded their flavor stability. It appears that heat stabilization of concentrates produced by high-yield juice recovery methods was more effective with cloud than with flavor.

Information developed in this study has commercial application, in that it emphasizes the desirability of keeping the product temperature low during distribution. It will also aid the distributor in assessing probable damage caused by unavoidable increases in temperature.

In another series of experiments, frozen concentrated orange juices, at different density levels, were stored at 20°, 15°, 10°, and 5° F. and evaluated for cloud and flavor stabilities. When fresh juices low in enzyme activity were made into concentrates, higher concentrations alone were effective in increasing cloud stability. From 43 to 60° Brix cloud stability increased with concentration with or without heat treatment, but the cloud stability of the juices was further increased by heat treatment at 150° F. Not only did the cloud stability increase with concentration but at the higher densities small increases in concentration increased stability more than equivalent increases at lower density levels. Taste panel evaluations of concentrates indicated very little improvement in flavor stability with increased concentration. The 150° F. treatment did not increase flavor stability consistently at any level of concentration. Concentration was more effective as a method of increasing cloud stability than as a method of increasing flavor stability.

The leaves of domestic muscadine grapes and of wild grapes were found to contain a water soluble material which will inhibit pectinesterase activity and add stability to the cloud in orange concentrate. Control of pectinesterase activity in this manner without heat treatment of citrus products may be of both practical and theoretical importance, but requires further investigation.

3. Development of Pulp-Fortified Grapefruit Products and New Grapefruit Based Beverages. Because red grapefruit represents a large portion of the total production (some 65 percent of the 1960-61 Rio Grande Valley citrus

crop), practical procedures have been sought for producing highly colored frozen grapefruit juice concentrates and other grapefruit drinks from colored grapefruit by fortification with pulp from the colored fruit. These products should have increased consumer appeal and provide new or extended outlets for the fruit.

Mid season and late season packs (1960-61) and an early season pack (1961-62) of pulp-fortified red grapefruit juice concentrates were prepared, stored, and evaluated for color, cloud retention and taste. The improvement of the color of the reconstituted concentrate by the use of high pulp cutback juice in the preparation of the concentrate was repeatedly demonstrated. The addition of this pulp had an adverse effect on cloud retention which could be overcome by heat treatment of either the low pulp evaporator feed juice (mid season) or the heat treatment of both the low pulp evaporator feed juice and the high pulp cutback juice (early and late season). The addition of this pulp also caused gelation which could be overcome by heat treatment of either the low pulp evaporator feed juice or the high pulp cutback juice, or both. There was no apparent detrimental effect on taste due to the heat treatment necessary to offset the adverse effect on cloud and gelation of addition of high pulp cutback juice. Due to the freeze of January 9-12, 1962, which prevented a full season's work, these observations should be rechecked through another season under carefully controlled conditions, when normal fruit becomes available. The 1960-61 findings showing the favorable possibilities of red grapefruit concentrate were factors in encouraging the construction of three new concentrate plants in the Rio Grande Valley prior to the freeze.

Preliminary experiments have been initiated to develop new drink formulations using grapefruit juice as a major component of blended drinks or punch concentrates. Grapefruit-based berry or fruit flavored drinks show promise. (S3 2-33).

4. New and Improved Products from Texas Oranges and Minor Fruits. During the past several years increasing numbers of orange trees have been planted in the citrus producing area of Texas. Data have been obtained on the seasonal variation and juice quality of Valencia, Hamlin and Marrs fruit to guide processors in the efficient production of concentrates and other juice products.

Variations in the juice quality of Valley-grown Valencia oranges were followed by weekly samplings of fruit from two locations for about 4 months of the 1960-61 season. The yield of juice showed little variation during the testing period. Acid values declined during the period; while Brix values increased sharply during the early weeks, leveled off during the mid season, and remained at about the same level for the last half of the period. The Brix-acid ratio increased during the test period, due primarily to the steady decrease in acid values. The solids-per-box and solids-per-ton values had the same trend of variation as the Brix values since the yields of juice were fairly constant. Little variation in juice quality and yield was noted between fruit from the two groves tested. The color of all samples was good. The trends of variation in juice quality were essentially the same as those reported for Florida Valencia oranges.

Similar type data were obtained for Hamlin and Marrs oranges harvested at weekly intervals from two locations over a 3-month period in the 1961-62 season. The low acid, Brix and color values noted for juice from Hamlin oranges

indicates that a high quality juice product could be prepared from this variety only by blending a large quantity of juice from another variety such as Valencia. Juice from the Marrs oranges showed higher Brix and color values, but the low acid values indicate that this variety should also be blended with a variety such as Valencia.

The juice yield, citric acid content, and ascorbic acid content of the oranges decreased rapidly after the freeze of January 12, 1962. Hamlin and Marrs, the more mature varieties on this date, showed the greatest loss, while Valencia, a later maturing variety, had the smallest percent of decrease. (S3 2-23).

An improved, inexpensive, and easily prepared guacamole (avocado salad mixture), which employs ordinary commercial cracker meal to improve the consistency of the thawed product, and which can be frozen and stored for as long as 12 months at 0°F. has been developed. The mixture may be prepared by a commercial processor interested in volume sales or by the housewife from her home-grown avocados. Such a product extends the outlet for avocados in the processed form.

Previous experiments had developed formulas for products in which separation of a watery phase after freezing and thawing was successfully retarded by using ingredients such as waxy rice flour, sodium alginate or other thickening agents. While these ingredients are suitable for the commercial processor, they are not readily available to the housewife. Now it has been found that the separation may be overcome simply by adding cracker meal, a common commercial product in retail distribution. (S3 2-23).

C. New and Improved Processing Technology

1. Application of Foam-Mat Drying to Florida Citrus. With the cooperation of the Florida Citrus Commission and the Western Utilization Research and Development Division, a complete integrated pilot plant for investigation of foam-mat drying of citrus juices to produce citrus powders of optimum flavor and stability was designed, installed, and placed in operation at the Winter Haven Laboratory. In the foam-mat process, a fluid material citrus concentrate, is mixed with a small amount of edible stabilizer. The mixture is whipped into a foam and then extruded as small ribbons onto a moving belt, and air dried.

Good progress has been made in research on foam-mat drying of orange concentrates, particularly in establishing maximum tolerable temperature and time relationships in drying, in relative humidity-moisture relationships in dried powders, and in initiating storage studies. Equipment modifications have been made to increase useful air temperatures and improve temperature control. Investigations initiated also include the evaluation of foam stabilizers with respect to their effects on flavor, stability, and reconstitution; inert gas packaging; secondary drying; volatile components of orange powders; and the exploratory preparation of grapefruit powder. Two studies completed are reported in the following paragraphs.

The equilibrium moisture contents of two "Foam-Mat" dried orange juice powder products were obtained in the lower range at relative humidity for 50°, 70°, 80° and 100°F. storage. One orange juice product was stabilized with 0.8% modified soya protein and 0.2% methyl cellulose on a solids basis, while the other contained 1% monoglyceride. In general it was indicated that a relative

humidity of about 6% would be satisfactory to handle monoglyceride powder of 1% moisture content, while even lower humidities would be required for modified soya protein stabilized powders. Both types of powders with 2% moisture content could be handled in 15% relative humidity, except modified soya protein stabilized material at 50° F. which would require a lower humidity. A 10% relative humidity was adopted for the handling of these powders, as this provides a margin of safety to cover such adverse conditions as dehumidifying equipment failures for brief periods, or overloading of this equipment because of excessively high humidities in the surrounding atmosphere. Both orange juice powder products have a tendency to cake when adsorbing moisture. From observations in processing this tendency increases as moisture content increases.

An evaluation of the effects of drying times and foam temperatures on the initial quality of the dried products was made. A modified soya protein-methyl cellulose foam stabilizer, found to result in better appearance of the powder and reconstituted juice, was used in place of the conventional monoglyceride type stabilizer. Maximum foam temperatures during drying were 160°, 170° and 180°F. Products dried at 160°F. for 11.7 to 26.2 minutes were of good flavor and varied in moisture content from 4.55 to 2.71 percent. Those dried at 170°F. for 10.5 to 13.1 minutes contained 3.99 to 3.37 percent moisture and were of good flavor. Flavor changes were observed in products dried for longer periods. Powders dried at 180°F. for 8.8 to 13.1 minutes contained 4.03 to 2.46 percent moisture and were of good flavor, while changes were observed in those dried for longer periods. The majority of the powders prepared in this study were of good flavor. Only those dried at the higher temperatures using drying periods in excess of 13 minutes differed in flavor from that of the reference control. (S3 2-32).

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AREA NO. 10 - VEGETABLES PROCESSING AND PRODUCTS - SOUTHERN LABORATORY

Problem. Although extensive progress has been made in developing stable, attractive, and convenient to use vegetable products, new and improved processed products must be developed and means of stabilizing perishable vegetables provided to minimize the adverse effects of seasonable surpluses and unfavorable markets, and to provide an adequate supply of good food for a growing population. Product quality needs to be improved and processing cost reduced through the adaptation and application of the latest technological developments and nutritional findings. For example, a major problem of the cucumber industry, since most of the crop is brine-cured, is to improve the curing process so that no loss occurs in the value of the cucumber during the brine-curing and storage process and the cost of processing is reduced. As another example, a precooked, dehydrated, sweetpotato product has been developed which has good shelf life, when sealed under an inert gas. It reconstitutes to a product having the characteristics of freshly cooked and pureed sweetpotatoes. Applied research on a pilot-plant scale is needed to obtain additional engineering and processing data applicable to commercial production. Basic research is needed to improve the quality and storageability of the product. There is a continuing need in the use of vegetables for processing to investigate the characteristics of the raw material as these characteristics are affected by climate, soil, cultural practices, breeding and the like. For example, celery, already an important flavoring ingredient, could become much more important if the factors and constituents responsible for the intensity, variableness, and stability of its flavor could be controlled in processing. Many vegetables grown in the Southern Region differ in their chemical and physical characteristics from the same crops grown in the more temperate regions; and several vegetable crops are grown almost exclusively in the Southern Region. More utilization research is needed to complement the Federal and State production research programs and to provide cooperation in the form of competition and processing studies.

USDA Program

The Department has a continuing long-term program involving biochemists, organic chemists, microbiologists, food technologists, and chemical engineers engaged in both basic and applied utilization research studies on vegetables of the Southern Region to develop new or extended uses for these commodities.

Research to develop basic information on chemical composition and physical properties of vegetables, their products and byproducts, is conducted as a basis for efficient research in developing new and improved food products and processing technology. Emphasis at the present time is on investigations of the flavor constituents in celery, carried out at the U. S. Fruit and Vegetable Products Laboratory, Winter Haven, Florida, to improve the quality of processed products in which whole celery, celery juice, and other celery constituents are used. This work is closely related to that of the Florida Agricultural Experiment Station at Gainesville, with which close liaison is maintained, particularly on the application of research results.

In the field of new and improved food products by processing of vegetables, research is being carried out at New Orleans, Louisiana, to improve or modify certain characteristics of the precooked dehydrated sweetpotato flake product with special emphasis on improvement of product acceptance and maintenance of

quality during storage. Close cooperation is maintained with the Louisiana Agricultural Experiment Station, which furnishes sweetpotatoes of known history, and industry and industry association. The Marketing Economics Division, ERS (under a formal memorandum of understanding with the Southern Division, the Louisiana Sweet Potato Commission, the Louisiana State Agricultural Experiment Station, the Louisiana State Department of Agriculture, and Red Star Yeast and Products Company) conducts market tests on promising precooked dehydrated sweetpotato flake products to determine their consumer acceptance and market potential. Research is also in progress at the U. S. Fruit and Vegetable Products Laboratory, Weslaco, Texas to develop new and improved processed products from vegetables of the Southern Region, including green beans, southern peas, tomatoes, beets and carrots. The Texas Agricultural Experiment Station and industry associations provide raw materials of known history for these studies.

Research on new and improved processing technology is conducted at New Orleans, Louisiana and at the U. S. Food Fermentation Laboratory, Raleigh, North Carolina. Pilot-plant investigations are being carried out at New Orleans on the production of a precooked dehydrated sweetpotato flake product to obtain engineering and other processing data applicable to commercial production. Processing variables being investigated include the effect of variety, curing, preheating, type of cooking, and type of packaging. The Louisiana Agricultural Experiment Station and industry associations are supplying potatoes of known history. This work is closely related to the work of the Eastern Utilization Research and Development Division to improve the quality of processed potato products. At Raleigh the objective of the research is to improve cucumber processing technology and the quality of the products. Current emphasis is on investigations of methods for the controlled fermentation of cucumbers by application of pure culture techniques to fermentation practices (including differential control of microbial species in natural fermentations by chemical and physical means) in order to reduce processing costs and improve product characteristics. The North Carolina Agricultural Experiment Station is cooperating in the design and execution of experiments concerned with the irradiation and other postharvest treatments to maintain or improve cucumber processing characteristics, and develop leads to improved methods of processing. The Michigan State University (Department of Microbiology) provides technical assistance in the controlled fermentation studies. The Eastern Utilization Research and Development Division is isolating and investigating the chemical nature of the material in grape leaves responsible for the inhibition of pectinolytic and cellulolytic enzymes, the types causing softening of brined cucumbers. The National Pickle Packers Association contributes support to the research and supplies raw material.

The Federal in-house scientific effort devoted to research in this area totals 10.0 professional man-years. Of this total 1.3 is devoted to chemical composition and physical properties, 2.6 to new and improved food products, and 6.1 to new and improved processing technology.

During the year a broad project involving investigations of the influence of various processing variables in improving processed cucumber products was terminated. It was replaced by a new line of work dealing with studies of methods for the controlled fermentation of cucumbers, with emphasis on pure culture techniques (under new and improved processing technology).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

Related programs of all State Experiment Stations and Industry and other organizations are reported by the Western Utilization Research and Development Division in Summary of Current Program and Preliminary Report of Progress.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Identification and Characterization of Flavor Constituent of Celery to Improve Processed Products. Continued good progress was made in characterization of flavor and odor constituents of celery. Basic information of this type is necessary for the proper study of celery processing methods and the intelligent selection of raw materials; and for the development of objective methods for estimating quality and total flavoring capacity that would enable the standardization of celery products by industry.

Many compounds have been identified in fractions obtained by distillation of expressed celery juice. Of these compounds, 3-isobutylidene- $\Delta^{5,7}$ -dihydrophthalide, 3-isovalidene- $\Delta^{5,7}$ -dihydrophthalide, 3-isobutylidene phthalide, and 3-isovalidene phthalide are believed to furnish the major flavor and odor notes. Sedanonic anhydride, which is the primary odorous material in celery seed oil has also been found to contribute to the flavor of celery. Other materials identified, and which contribute to the overall aroma of celery are: d-limonene; myrcene; iso-butyric acid; n-valeric acid; pyruvic acid; palmitic acid; guaiacol; n-octanal; n-undecanal; neral; n-heptanol; n-octanol. Acetaldehyde, diacetyl, and a number of alcohols and esters have been tentatively identified. It has been found that while many of the above compounds are normally thought of as being highly objectionable, their odors become less objectionable and even pleasant when in sufficient dilution. (S3 5-17).

B. New and Improved Food Products

1. New and Improved Canned and Dehydrated Sweetpotato Products. Research to improve product quality and storageability of precooked, dehydrated sweetpotato flakes was continued. The importance of storage of the flakes in atmospheres low in oxygen (less than 2%) has been further verified by experiments where flakes were sealed in air and at intermediate oxygen levels (3 to 10%), and by measuring the oxygen absorbed by these sample preparations from the gas mixtures in sealed containers during storage. Storage stability at 100°F. in low oxygen atmospheres was limited to 15 months, after which an objectionable taste was reported by panel evaluation. The use of antioxidants and synergists including butylated hydroxyanisole, butylated hydroxytoluene, propyl gallate, alpha-tocopherol, citric acid, and sodium acid pyrophosphate, singly and in various combinations up to 900 p.p.m., to attempt to stabilize sweetpotato flakes sealed in air has not been practically successful, although a delay of poor flavor onset (up to 48 days) has been demonstrated.

Numerous samples of dehydrated sweetpotato flakes, with evaluation cards, have been distributed to interested individuals and organizations throughout the United States to obtain consumer reaction. Of approximately 2,000 evaluations received, about 80% of the people liked the flake product as well as or better

than fresh sweetpotatoes, and over 90% liked the product as well as or better than canned sweetpotatoes. In tests conducted in cooperation with ERS, 102 consumer institutions were canvassed in Cleveland, Ohio, and New Orleans, Louisiana (51 in each city). Of each group of 51, 44 were restaurants and 7 were institutions such as elementary or high schools, boarding schools, childrens' day nurseries, hospitals and old folks' nursing homes. The reconstituted sweetpotato flakes were offered to the consumer as "a new recipe." A highly favorable reaction was indicated by management, kitchen help and consumers in restaurants and other types of institutional outlets. It is anticipated that this product can bring about changes in previous patterns of use and provide some of the impetus necessary to bring about a reversal in the decline in sweetpotato consumption.

Present research involves studies (1) to enable the processing of uncured sweetpotatoes by evaluating the use of commercially available amylolytic enzymes as a process adjunct to replace the curing step, and (2) to evaluate hydrophylic colloidal materials (gums, dextrine, dextrans and modified starches) for the improvement (stabilization) of sweetpotato flakes (S3 5-19).

2. Development of Modified Processing Procedures for New Varieties of Texas Vegetables. In cooperation with the Texas Agricultural Experiment Station, another season's study was made of the effects of row spacing on green beans for processing in the lower Rio Grande Valley area. The results confirmed previous published findings of the cooperative research, demonstrating substantial differences in acre yields but no measurable effect on factors affecting processed quality. Spacing the rows at 12 inches as compared with 38 inches increased production as much as 4707 pounds per acre for Corneli 14 variety and 2604 pounds for Tenderwhite. With 6-inch spacing the increase was less than that for 12-inch, due to overcrowding of plants associated with adequate rainfall and luxuriant growth. Spacing had no measurable effect on seed percentage, fiber percentage, or color; and a sensory panel could detect no difference in the canned pods due to row spacing.

Further experiments were conducted on firming the tissue of canning tomatoes in order to reduce peeling loss and increase drained weight, with resultant increase in the yield of cases of canned product per ton of fresh fruit. Previous work at Weslaco had indicated that tomatoes blanched in a boiling 2 percent calcium chloride solution for 45 to 60 seconds (until the skins cracked) increased in drained weight from 2.2 to 8.8 percent and in wholeness percentage from 17.5 to 27.6 over fruit blanched in water alone. In the present experiments calcium chloride was added to the blanch or peeling water; and the skins of the tomatoes were pricked to increase the uptake of calcium. Preliminary observations during the hand peeling operation indicated that the pricked and calcium-treated tomatoes were slightly firmer than those untreated, and that the skin of the pricked fruit would split and tear off in smaller pieces. Appraisal of the practical value of the combined treatment awaits completion of evaluation tests on the trial packs so prepared.

Evaluation of canned packs of 20 varieties and selections of canning type beets from 5 seed sources revealed only minor differences in color or flavor, pH, percent acid, and refractive index. Selection by a grower of one of the varieties or strains tested would be influenced more by yield, size, and possibly percentage black spot of the raw stock, rather than by differences in quality of the processed products.

Limited effort has been made to develop a precooked, dehydrated carrot flake similar to the precooked, dehydrated sweetpotato flake. A major difficulty encountered to date is that of producing a flake with high enough density. It is hoped this problem may be solved by incorporation of different kinds of food additives, mostly of the hydrocolloid type. Limited storage tests conducted to date indicate that carrot flakes, like sweetpotato flakes, must be packaged under nitrogen. It may be that the additives to be evaluated for increasing flake density will also increase stability of the flakes in air. This will have to be determined by further experimentation. (S3 5-16).

C. New and Improved Processing Technology

1. Processing Investigations to Improve Quality and Reduce Costs of Canned and Dehydrated Sweetpotato Products. A sweetpotato flake pilot plant was designed, constructed and operated at the Southern Regional Research Laboratory to obtain processing and other engineering data necessary for commercial adaptability and for conducting cost calculations, and to supply adequate samples of the instant precooked sweetpotato flakes for evaluation, including a market study by ERS. Since the processing is continuous and the equipment is of commercial type, the pilot plant is considered to be a prototype for a commercial installation.

One processor started commercial production of the flakes during the late 1961-62 processing season and has reported plans to double their capacity during the 1962-63 season. Another company is reportedly planning to install equipment and start operations to produce flakes in early 1963. Several other companies in Louisiana, Mississippi and North Carolina have expressed considerable interest in the flake product and process.

After test runs were made in the SU pilot plant to effect necessary adjustments and modification of equipment for smooth and efficient operation, systematic experimental runs were conducted to study factors such as effect of preheating, methods of cooking, use of cured versus uncured sweetpotatoes, and use of different sweetpotato varieties. Some important findings were: (1) data indicates that the preheating step may be eliminated; (2) recovery of 8 to 10% solids, normally lost by steam cooking, is possible by using a water-cooking procedure; (3) "self-curing" of sweetpotatoes at ambient conditions is not practical, and other methods such as enzyme treatment will be necessary to process uncured sweetpotatoes; (4) Centennial and Nema-gold sweetpotato varieties do not produce good flakes when processing conditions such as those found best for Goldrush are used.

Cost estimates have been made for producing flakes in hypothetical "all-new" plants having processing rates of 6,000, 12,000 and 18,000 pounds of sweetpotatoes per hour. Costs range from 40.7 to 72.9 cents per pound of product based on a raw sweetpotato price of 1 cent per pound.

A contract with the QMC has been fulfilled for engineering and cost reports and for supplying them with 750 pounds of flakes. Pilot plant production of 6,000 pounds of flakes for a cooperative institutional market study (SU, ERS, and Red Star Yeast and Products Co.) was also completed.

Study of the flexible packaging of the flake product has been started. Successful flexible packaging is required to "tap" the retail market and to expand commercialization of the product and process. (S3 5-19).

2. Processing Investigations to Improve Quality and Reduce Costs of Fermented and other Vegetable Products. Recent research to improve cucumber processing technology and the quality of the products has been concerned principally with studies of: (1) Influence of different preprocessing temperatures and humidities on microbial, enzymatic and physical changes of stored pickling cucumbers, (2) Cucumber softening enzyme inhibitors, (3) Controlled fermentation of cucumbers, and (4) Suitability of new cucumber varieties for pickling.

A second season's tests on the changes occurring in pickling cucumbers exposed to different preprocessing temperatures and humidities have confirmed and expanded observations made during the 1959 season. Of the various temperature and humidity (RH) conditions observed during the 2-year study, that of 50°F. with 90-95% RH would be considered to be the most desirable for cucumber storage and transportation; microbial development and softening enzyme activity were almost wholly suppressed and moisture loss from the cucumbers was minimized. The basic information now appears at hand to provide a better understanding of certain microbial, enzymatic and physical (weight loss) changes that take place with pickling cucumbers held in a prescribed and precise environment with respect to temperature and humidity conditions. With this specific information it would now seem possible for those concerned to design better handling, storage and shipping equipment and facilities for cucumbers. Such developments would reduce the large economic loss often associated with handling, transportation, and storage of pickling cucumbers.

In further work, with the cooperation of the Eastern Utilization Research and Development Division and the North Carolina Agricultural Experiment Station, the water-soluble leaf extracts from 61 plant species in 32 families were screened for their ability to inhibit two hydrolytic fungal enzymes, cellulase and pectinase, which are responsible for the softening spoilage of cucumbers brined under commercial conditions. Leaf extract from 29 species inhibited pectinase and extracts from 14 inhibited cellulase. The leaves from muscadine grape, persimmon, dogwood, blueberry, sericea, blackberry, raspberry, and rose were considered good sources for the pectinase inhibitor as measured against cucumber-flower pectinase and a commercial pectinase. In general, cellulase inhibition by the different plant species was less pronounced than that observed for pectinase. The first five species listed above gave strong inhibition of cucumber-flower cellulase. Muscadine grape and persimmon were the only two species which inhibited the commercial cellulase enzyme 19AP, and then only moderate to weak inhibition was obtained. The finding that the forage crop sericea (*Lespedeza cuneata*) is a good source of the inhibitor for pectinase and cellulase is also of interest in connection with the use of the forage for livestock feed.

Subsequently, a number of breeding selections of sericea were tested for their softening enzyme inhibitory activity throughout a five-month growing season in North Carolina. Certain selections retained a high inhibitor content throughout the growing period whereas other lines remained consistently low. Tests are being conducted on the stability of the inhibitor substance in sericea during the several operations required to prepare commercially dehydrated material in pellet form.

Brining tests in 50-gal. barrels were started at a commercial pickling plant to determine the influence of added sericea extracts on the brine fermentation of cucumbers, particularly with respect to inhibition of the added softening enzyme pectinase and resultant firmness quality of the cured brine-stock. Brine samples taken during the active fermentation from the 21 barrel

fermentations showed that the pectinase activity of the sericea added lots was effectively reduced. The brine acidity of all lots reached 0.70-0.80% (lactic) with brine pH's all very close to 3.5. Evaluation of the brined material as to firmness, bloater content and acceptability for commercial use will be made at a later date, coincident with completion of curing. (S3 5-18).

Observations were made on 60 pure culture fermentations, including replications and controls, in research on controlled fermentation of cucumbers. Cultures of lactic acid bacteria representing species associated with cucumber fermentations were examined for their fermentative ability in salt brine (3-6%). The test cultures grew rapidly and reached populations of 30-380 millions per ml. in 40 hrs. No evidence was obtained that other microbial groups grew in the brines during the observation period. Final brine acidities reached 0.45-0.50% lactic acid for cultures of Ped. cerevisiae and L. brevis, with brine pH's of 3.7 - 3.40. Acid production of strains of L. plantarum was higher, ranging from 0.65-0.95%, with brine pH's of 3.35-3.20. Observations on the brinestock pickles from these fermentations demonstrated a difference in color and odor for strains of the same species, particularly Ped. cerevisiae, a common species in commercial brines. Certain strains of this species gave the brine a stale, hay-like odor and the pickles revealed an off color, with evidence of bloating. Successful preparation of pure culture dill pickles was accomplished in glass containers and in No. 10 tin cans and in the presence or absence of spices and garlic.

This work has emphasized gaining complete control of the fermentation and selection of the most desirable strains and species of lactic acid bacteria for use. Valuable basic information on the behavior of these organisms in brines has been obtained. Specific fermentation differences of individual species of lactics, as well as differences between strains of the same species, represent important findings vital to the final selection of lactics for use in controlled cucumber fermentations. These pure culture studies are being elaborated and the data applied to the development of pure culture processed pickles and processing procedures. (S3 5-20).

Assistance was again rendered plant breeders at the Arkansas, South Carolina and Michigan Agricultural Experiment Stations in evaluating several hundred new cucumber varieties for brine-stock purposes. New and improved varieties are particularly needed in the South, because the chief variety now in use (Model) leaves much to be desired. This cooperative research with breeders, the pickle industry and the National Pickle Packers Association, has culminated in the release during the past year of three new pickling cucumber varieties, namely: "Southern Pickler" by the Arkansas Agricultural Experiment Station; "Pixie" by the South Carolina Agricultural Experiment Station; and "Spartan Dawn" by the Michigan Agricultural Experiment Station. The first two varieties are intended to meet packers' needs in southern production areas; the third was bred for northern growing areas. This research accomplishment will mean increased benefits to farmers, processors, and consumers. (S3 5-16).

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AREA NO. 11 - NAVAL STORES PROCESSING AND PRODUCTS

Problem. More uses for turpentine, rosin and pine gum need to be developed through research to provide new industrial markets for current and anticipated production of gum naval stores. These gum naval stores products face serious competition for markets from research-developed products, especially those from the chemical and petroleum industries. As an illustration, turpentine has lost substantially all of its industrial solvent market to low-cost petroleum based solvents. New fundamental information about the chemistry, composition and properties of pine gum, rosin and turpentine is needed to fully exploit their unique characteristics in the production of new and improved industrial products having utility as industrial chemicals, polymers, plastics, elastomers, resins, plasticizers, surface coatings, textile finishes, odorants, insecticides and herbicides. There is also a serious need to improve existing processes and develop new processing technology for the industry.

USDA PROGRAM

The Department has a continuing long-term program carried on at Olustee, Florida, involving organic chemists and a chemical engineer engaged in both basic and applied research to discover and develop new and improved uses for pine gum and its products. In basic research on the chemical composition and the properties of gum naval stores materials the emphasis is on the isolation and characterization of some of the unidentified components of pine gum, rosin, and derivatives to obtain information that will aid in the further industrial utilization of gum naval stores. The U. S. Forest Service cooperates by supplying samples of pine gum. Informal cooperation is maintained with industry. In research to develop new and improved industrial products from pine gum, rosin, turpentine, or their components, conversion of the resin acids derived from gum rosin and pine gum to new polyfunctional products by reaction with suitable chemicals is under investigation to develop intermediates for production of resins, plastics, plasticizers, and other products. Another research approach involves the condensation of the unsaturated (olefinic) materials present in pine gum with certain reactive chemicals (dienophiles) to produce industrially useful chemicals. The photochemical addition of chemicals to resin acids is being studied to produce new chemicals of potential utility in the fields of surface active agents, textiles, paper, and plastics. Other research includes investigations to convert turpentine and rosin into polymerizable products suitable for making new polymers, plastics, and resin; to prepare chemical intermediates and modified rosin compositions by hypochlorite reaction of rosin and resin acids; to convert rosin, resin acids, and resin acid derivatives to polyfunctional compounds useful in plastics, resins, and surface coatings by formaldehyde addition and subsequent reactions; and to produce reactive chemical intermediates from turpentine by reaction with inexpensive low molecular weight compounds. The Pulp Chemicals Association supports a Fellowship at the Naval Stores Laboratory for the purpose of conducting research to develop a suitable method for determining rosin and rosin derivatives in protective coatings, a necessity if rosin is to be allowed in certain types of these coatings from which it is now excluded. Informal cooperation is maintained with other agencies and industrial firms to evaluate promising research products for specific properties and end uses. Close consultation is maintained with the gum naval

stores industry and its associations. An important phase of current research on new and improved processing technology is the development of a commercially feasible process for isolation of the pure resin acid, levopimaric acid, from pine gum. This is a major, reactive resin acid which should be useful as a chemical intermediate in many industrial applications. Research is also being conducted on processes for the production of paper sizes directly from pine gum. Paper companies and other industrial firms cooperate informally in the evaluation of the new types of sizes.

The Federal scientific research effort in this area totals 15.0 professional man-years. Of this total 2.0 is devoted to chemical composition and physical properties; 11.0 to new and improved industrial products; and 2.0 to new and improved processing technology.

The following lines of work were terminated during the year: (1) Investigation of processes for the conversion of pine gum to rosin and resin acid composition having a high levopimaric acid content; and (2) a broad investigation of the development of polyfunctional compounds from rosin and pine gum (all under new and improved industrial products).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported no work in this area.

Industry and other organizations conduct research on naval stores utilization at the rate of about 5 to 7 man-years annually. The wood naval stores industry conducts about 90 percent of the industrial research on naval stores, with one large industrial concern accounting for 70 to 80 percent of it. The gum naval stores industry and the pulp chemicals industry each do about 5 percent of the total. It is estimated that 80 to 90 percent of the total industrial research in this area is concerned directly with new and improved industrial products. This includes product evaluation for various end uses, process development, and formulation research aimed at using basic company products in new end uses or meeting specific requirements of a customer.

Research is aimed at increased use of naval stores derivatives in virtually every field from perfumes to rubber reclaiming. Very few of the results of industrial naval stores research are made public except in the form of patents. Industry, in general, cooperates with the Department by supplying reference compounds and starting materials. Informal exchange of information is also mutually beneficial but the major research organizations are usually unwilling to discuss details of their current research program.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Composition and Physical Properties of Pine Gum. Research is in progress to isolate and characterize some of the unidentified components of pine gum and its derivatives to provide basic information that will aid in the further industrial utilization of gum naval stores products.

To facilitate the identification and characterization of some of the minor components of pine gum, the periodate-permanganate oxidation of several resin acids and resin acid derivatives of known structure has been studied.

Oxidation techniques and separation of the oxidation products obtained by these techniques have been worked out. Ketodicarboxylic acids have been isolated and characterized from the oxidations of neoabietic and palustric acids. The acid from neoabietic acid appears to be closely related to some of the plant growth hormones. Progress has also been made in the study of the oxidation products of levopimaric acid. An understanding of the oxidation products of the resin acids will aid in avoiding changes during processing and handling that could affect the quality of the products and also give us new basic information on the chemistry of pine gum and its components. A new resin acid has been isolated from slash pine gum which accounts for about 4 to 6 percent of the acid portion of the gum. The new acid, which was obtained in crystalline form by vacuum sublimation is unusually sensitive to oxidation. It appears to be a monobasic diterpene acid. This new acid is not present in any detectable quantities in longleaf oleoresin. Its characteristic of reacting slowly with maleic anhydride at room temperature would indicate that slash and longleaf rosin at low levels of maleic modification would have a considerable difference in composition. This could explain some of the differences encountered in the preparation of fortified paper size from rosins from different sources. The ease of polymerization of this acid and its resistance to crystallization probably explain much of the difference between rosin obtained from slash trees and that obtained from longleaf. (S5 2-36).

B. New and Improved Industrial Products

1. Development of Intermediates for the Production of Resins, Plastics, and Plasticizers from Pine Gum and its Components. Research is being carried out to convert turpentine and rosin into products which will homopolymerize and copolymerize with other polymerizable substances to produce new polymers, plastics, and resins to expand utilization of pine gum commodities. Investigation of the polymerization of the more promising derivatives will be carried out under contract at the University of Arizona. Continued research on vinyl monomers has led to the preparation of the vinyl ester of morpholine amide of pinic acid in satisfactory yield. A homopolymer from this was a brittle glass. The addition of chlorine to alpha-pinene ozonide in aqueous methanol gave methyl pinonate, opening up a new product possibility for ozonization of olefins. Pinonic acid esters have been condensed with various amines by reductive amination to produce new derivatives. Acetylenic alcohols have also been made from pinonic acid and homoterpenylmethyl ketone. All of these derivatives of pinonic acid should have good potential industrial value as intermediates for polymers, plastics and resins, particularly since an industrial firm is currently going into pilot-plant scale manufacture of pinonic acid. (S5 2-38).

The production of chemicals from terpenes present in or derived from turpentine and pine gum, for use in the preparation of odorants, herbicides, plastics, plasticizers, and other products, should improve the position of these naval stores materials. The photosensitized oxidation of limonene and 3-menthene is being studied as a means of producing reactive chemical intermediates from turpentine. The oxidation of purified and commercial limonene yielded products which were indistinguishable, establishing the suitability of the commercial material for this purpose; 3-menthene was converted to a mixture of alcohols. In other experiments, p-toluenesulfonic acid showed promise as a reagent for converting terpenes like 1- and 3-p-menthene,

alpha-pinene, and limonene to interesting hydrocarbon dimers. An improved method of purifying β -phellandrene, the third largest component in gum turpentine, was developed and should promote the efficient utilization of gum turpentine by fractionators.

Base catalyzed isomerization and dehydration of selected alcohols will be studied as a route to polymerizable monomers from turpentine. Research on the reaction products of dienophiles and terpenes will also be emphasized. (S5 2-40).

2. Addition of Chemicals to Rosin Acids With Emphasis on Photochemical Methods to Produce Chemicals Useful in Manufacturing Surface Active Agents, Textiles, Paper and Plastics. Studies of the photosensitized oxidation of the resin acids of rosin were continued as a basis for production of new chemicals having potential value in industrial applications.

Research on the photosensitized oxidation of neoabietic acid was completed during the period. Based partly on relationships established between the photoperoxides obtained from the photosensitized oxidation of neoabietic and levopimaric acids, absolute configurations have been suggested, others confirmed, interrelationships established, and the conclusion drawn that all seven of the major resin acids of known structure found in pine gum have the same absolute configurations about the asymmetric "backbone chain," namely C-1- β -methyl, C-11- α -hydrogen, C-12- β -methyl, and C-13- α -hydrogen (with the one exception of a C-13- β -hydrogen in isodextropimaric acid). The stereo-chemical relationships established in this work are basic to a really complete understanding of all the chemical changes and reactions of the resin acids of pine gum and rosin, and will undoubtedly pay off in terms of the applied chemistry of pine gum and rosin in the future.

From a reinvestigation of the ultraviolet irradiation of levopimaric acid, it appears that the reaction product is not a dimer as previously supposed, but rather a new type of resin acid derivative, namely a 6, 14-bridged cyclobutene derivative. Due to the presence of a fourth or "D" ring, this valence tautomer may more closely resemble the steroids in chemical and physiological properties than do the resin acids. Preliminary studies of the ultraviolet irradiation of palustric acid indicate that bridging also occurs with this acid.

The photosensitized addition of several reagents other than oxygen to levopimaric acid has apparently been successfully obtained. It should be possible to produce new and potentially useful chemicals in this way. A two-step process developed for preparation of a dibasic acid from levopimaric acid (by irradiation with ultraviolet light, followed by ozonization) provide a potentially important product for manufacture of laminating resins in the field of plastics. Photosensitized oxidized gum rosin and pine gum were made and will be evaluated by industry as vulcanizing agents for rubber stocks, synthetic rubbers and polyethylene.

In further studies of the photosensitized addition of various reagents to levopimaric acid, a process has been discovered whereby this resin acid can be converted to dehydroabietic acid by treatment with light plus sensitizing dye. Sulfur-containing products produced by the photosensitized reaction of levopimaric acid with sulfur and sulfur dioxide should have utility in

the fields of surface active agents, textiles, paper, and lubricating oil additives. (S5 2-37).

3. Conversion of Turpentine and Rosin Acids into New Polymers, Protective Coatings and Resins. The resin acids of gum rosin and pine gum are monofunctional, i.e., they contain one carboxyl group. Conversion of these monofunctional substances to new polyfunction products by reaction with suitable chemicals is under investigation to develop intermediates for production of resins, plastics, plasticizers, and other industrial products.

Investigation of the conversion of levopimaramide to levopimaral isocyanate, a potentially important industrial chemical, by the Hoffman reaction (KBr) has led to the observation that an unexpected isomerization occurs, presumably caused by alkaline hypohalite, and abietal isocyanate is formed. This probably explains the failure in earlier work to obtain solid derivatives from what was believed to be levopimaral isocyanate. From the levopimaramide a product was obtained containing 60-70 percent of levopimaral isocyanate and 30-40 percent of abietal isocyanate. Modification of the reaction conditions in the Hoffman reaction made possible the preparation of levopimaral isocyanate in a high state of purity.

It has been found that esterification of sodium resinate with methyl chloride in nonhydroxylic solvents gives essentially quantitative yields. This reaction can be applied to the esterification of pine gum to give a different type of ester gum.

By reacting the sodium salt of methylolated rosin (formaldehyde modified rosin) with methyl chloride, the corresponding methyl ester was prepared. Reduction of the ester yields the expected dimethylol derivative. The successful reduction of the methyl ester has completed the development of a process for the preparation of a potentially cheap, high molecular weight glycol from rosin. Preliminary tests indicate that precipitation of the sodium salt of resin acids from pine gum may be a good route to high grade paper size.

A detailed investigation of the reaction of formaldehyde and rosin has been started. (S5 2-33; S5 2-43).

Research was continued to develop new naval stores derivatives of value as resins, plasticizers, and other industrially useful chemicals by the condensation of the olefinic materials present in pine gum with reactive dienophiles.

Polyester resins with good properties and potentiality have been produced from several dibasic acid derivatives obtained by reaction of pine gum components with dienophiles. Those prepared from rosin-derived dibasic acids are pale amber-colored materials with good hardness and wetting ability for glass fibers in laminates. The resins from terpene derivatives are hard and almost colorless. These products have excellent compatibility with styrene and polystyrene. Preliminary evaluations of a series of alkyl esters of di- and polybasic acids prepared from Diels-Alder adducts of pine gum indicate that they may be useful as softeners and plasticizers for nitrile rubber.

Under certain conditions of reaction of fumaric acid with the turpentine in pine gum, fairly good yields of the mono-bornyl ester have been obtained.

Fumaropimaric acid also reacts with alpha-pinene to form a mono-bornyl ester. The direct esterification of turpentine during its reactions with fumaric acid provides an economically attractive method for obtaining useful esters from naval stores derivatives. The preparation of the allyl esters of fumaropimaric acid is also being investigated. A product has been obtained which can be readily polymerized to a hard resin. Tetracyanoethylene adducts of all of the abietic type resin acids have been prepared. Use of this and other nitrile-containing dieneophiles offers a route to synthesizing new polybasic acids and polyfunctional amines.

Good progress has been made in developing high quality unsaturated polyester resins from several naval stores derivatives. Products obtained by partially and completely modifying rosin with β -propiolactone were used in preparing unsaturated polyesters. Copolymers of these esters with styrene have been evaluated by a large producer of polyester resins and found to compare favorably with commercial products. Three polyesters prepared with turpentine as a basic component and copolymerized with styrene were found to be acceptable. A turpentine-maleic anhydride polyester was copolymerized with styrene to give a highly flexible rubbery casting. (S5 2-34, S5 2-42).

Polymers having a wide variety of properties have been prepared from hydronopoxyalkyl esters and other monomers in contract research at the University of Arizona. Emphasis has been on hydronopoxyalkyl acrylates. Copolymers were made using these monomers and styrene, acrylonitrile, butadiene and vinyl chloride. Interesting, tough, rubber-like terpolymers resulted when equal amounts of hydronopoxyamyl acrylate, butadiene and acrylonitrile were emulsion polymerized.

A large concentration of rosin is undesirable in certain types of surface coating vehicles and Federal Specifications TTR 266 now specifically exclude rosin derivatives. If there were a satisfactory procedure for determining the rosin content, specifications could probably be modified to permit the use of small quantities of rosin in the protective coatings. Research was initiated to develop such an analytical procedure. The Pulp Chemicals Association supports a fellowship for the work.

A modified Libermann-Storch colorimetric method has been developed which combines simplicity and accuracy in the determination of rosin and diene-type resin acids in the concentration range of 10-150 micrograms. The method should have industrial application in areas related to rosin chemistry where there is a need to determine the amount of unreacted abietic type acids present.

Valuable information has been obtained concerning the composition and chemical behavior of the "rosin acid" fraction of tall oil fatty acids. The knowledge gained will contribute much to the development of needed analytical methods for rosin and rosin derivatives in protective coatings. (S5 2-39).

C. New and Improved Processing Technology

1. Processing Investigations to Produce Naval Stores Products of Improved Quality at Lower Costs. By preparing paper size directly from pine gum, without handling of rosin as such, it should be possible to produce a size more economical than those made from gum rosin by present procedures.

Such a pilot plant process for preparation of paper size directly from pine gum was developed. This process consists of distilling turpentine from partially neutralized pine gum to produce a paste size. Conventional and maleic modified paste and dry sizes were prepared which had sizing efficiencies comparable or superior to commercial materials. One industrial concern has recently requested samples of sizes made from pine gum for evaluation purposes. They are reportedly interested in possible commercial production of some variation of sizes from pine gum.

A procedure was developed for the isolation of pure levopimaric acid from pine gum in yields substantially better than obtained by other reported procedures. In this procedure, the resin acids were precipitated from an acetone solution with 2-amino-2-methyl-1-propanol. The resin acid-amine salt was purified by recrystallization in methanol and liberated with phosphoric acid to obtain the pure levopimaric acid.

A large bench scale process was then developed for the isolation of levopimaric acid in which the turpentine and residual rosins were recovered. The residual rosins were recovered from the resin acid-amine salts by removing the amine on an ion-exchange column. The amine was then recovered from the column for reuse. The residual rosins were of two types; one having a higher than normal portion of neutrals and one having no neutrals. The process has commercial value because there should be a market for these products as well as pure levopimaric acid.

A simpler process for the isolation of the pure levopimaric acid from long-leaf pine gum has been achieved by the use of a limited amount of amino-propanol (about 1 equivalent for each mole of levopimaric acid present in the gum) rather than an excess based on the total resin acids. There is less color degradation on the recovered rosin, less amine to recycle, and the over-all yields appear to be better. These advantages over the older process should make the process more attractive industrially. Work is currently underway on slash gum. (S5 2-32; S5 2-41).

PUBLICATIONS REPORTING RESULTS OF USDA AND COOPERATIVE RESEARCH

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New and Improved Processing Technology

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AREA NO. 12 - PROCESSING AND PRODUCTS - SUGARCANE

Problem. Quotas established by the Sugar Act effectively prevent the accumulation of surpluses by limiting production to estimated requirements at stable, low prices for sugar. Prices received by farmers of the United States and Puerto Rico for sugarcane are based upon the recoverable sugar content of the cane; and the rising costs of production and processing make imperative the more efficient recovery of increased amounts of sugar to provide adequate returns for both processors and growers. Currently recovery of 75% of the total sugar in the cane is considered satisfactory in Louisiana, and about 83% in Puerto Rico and Hawaii. Improved processing methods could increase the recoverable sugar to at least 85% in Louisiana and over 90% in other areas. The development of more efficient processing methods depends in turn upon the acquisition of adequate data on the quantitative composition of juices extracted from sugarcane, and of materials processed to recover sugar. The chemical industry provides a promising potential for the utilization of additional sugar since more than 15 billion pounds of chemical products are produced annually and sold to every section of American industry. More information is needed on the chemistry and properties of products from sugar to expand their utilization and on the application of these derivatives in the production of plastics, protective coatings, emulsifiers, detergents and the like.

USDA PROGRAM

The Department has a continuing long-term program involving at the Southern Utilization Research and Development Division organic chemists and chemical engineers engaged in basic research on the composition and properties of sugarcane, sugarcane juices and derived products, and in applied research directed to the development of new and improved sugarcane processing technology.

Basic and exploratory studies are being carried out at New Orleans, Louisiana, on the composition of sugarcane and sugarcane juices as a basis for developing more efficient methods for economical production of high grade end products. Materials used in this research are being obtained from cane processed for pilot-plant experiments in cooperation with the American Sugar Cane League.

Research on new and improved processing technology is being conducted at New Orleans, Louisiana, and the Audubon Sugar Factory (Louisiana State University), Baton Rouge, Louisiana, to develop on a pilot-plant scale novel and more effective means of clarifying sugarcane juice, and improved methods of processing and purifying sirups to obtain greater recovery of raw sugar of higher quality at lower costs. At New Orleans, and at the U. S. Sugarcane Products Laboratory, Houma, Louisiana, investigations are being conducted on the composition and variations in the concentrations of nonsugar constituents of the juice in relation to efficiency of processing, recovery, and purification of sugar as a basis for devising improved processing and refining methods. This research is planned and conducted in close cooperation with the American Sugar Cane League. Sugarcane for the work is furnished by the League and use of the Audubon Factory for milling of the cane through the cooperation of Louisiana State University. Informal cooperation is maintained with the industry in evaluating quality of raw sugar and economic aspects of new processing methods.

The Federal scientific effort at the Southern Division devoted to research in this area totals 9.0 professional man-years. Of this total 2.8 are devoted to chemical composition and physical properties and 6.2 to new and improved processing technology.

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

State Experiment Stations in 1961 reported a total of 6.4 professional man-years effort in this research area, 5.6 being on chemical composition and physical properties, and 0.8 on new and improved processing technology.

The work on the chemical composition and physical properties of sugarcane is directed along two lines. Chemical studies related to the quality of sorgo juice for sirup and sugar production are conducted to evaluate various factors that influence manufactured quality. This work is done in cooperation with ARS. Microbiological studies related to the utilization of molasses are also underway. These studies include compositional determinations along with other phases involved in a search for new strains of organisms that better satisfy needs of alcoholic, lactic, citric and acetic fermentations. Optimum conditions under which microorganisms used in these fermentations may carry out the desired transformations are sought.

New and improved processing technology is being developed from several standpoints. Fermentation processes for rum manufacture are being studied to develop pilot-plant fermentation procedures for use in fermenting as efficiently as possible molasses mashers to produce high-quality rums. Another program involves studies on distillation processes for the production of rum. In this study, pilot-plant distillation equipment and procedures for use in efficient distillation are under development. Research directed toward purification of raw sugar by ion-exchange treatment has been conducted in cooperation with USDA. It sought to determine by the use of ion-exchange procedures the possibility of producing sugars that may be utilized in the production of hard candies and similar products without further purification.

Industry and other organizations expend an estimated 127 professional man-years effort per year on research in this area. Of this total about 20 is by processors, 87 by sugar refiners, and 20 by industry-supported organizations.

Only three firms processing sugarcane conduct organized utilization research. Hawaiian processors, through the Hawaiian Sugar Planters' Association, have conducted development work on uses of bagasse and are currently investigating the extraction of sugar by diffusion in large scale experiments. With limited basic studies of composition incidental to this research, work of their Experiment Station accounts for two-thirds of the industry effort in this field. Uses of bagasse have been investigated by one sugar corporation, in addition to experimentation to solve processing problems. Another sugar company conducts research on the use of sugar as well as bagasse in producing plastics, coatings, and similar products.

Eight sugar refining firms, and one user-refiner, are engaged in research on a wide range of problems, with major activity (2/3) on process, and the balance on product improvement and development. Information is exchanged with all of these firms, and a majority cooperate informally but closely in applying results of Southern Utilization Research and Development Division research on ion-exchange, on the composition of juice and raw sugar, and on impurities in

refined sugar. Examples of projects undertaken range from engineering of radically new, continuous processing equipment for decolorizing, developed by a sugar refiner with a research staff of 23, to pilot plant development of sucrose ester production by another firm with a staff of 6 professional workers.

The industry supports two organizations engaged exclusively in utilization and in process improvement research, and one which conducts limited fundamental research incidental to its routine operations. The Sugar Research Foundation, operating through grants or contracts in private and public institutions, carries on work equivalent to about 10 man-years which is divided equally between the development of food uses, and that of industrial uses of sugar. It receives major support from the cane sugar industry, but includes processors of sugar beets as members. Cane sugar refiners maintain the Bone Char Research Project at the National Bureau of Standards for broad investigation of the application of char, or other decolorizing agents, and related operations in purifying sugar. About 2 man-years are devoted to fundamental research on elucidation of the chemical composition and origin of colored impurities in raw sugar and molasses by the New York Sugar Trade Laboratory, maintained primarily for referee analyses in trading. As the work at both the Bone Char and Sugar Trade Laboratories parallels the Southern Utilization Research and Development Division's studies of juice composition and raw sugar quality, continual exchange of information and closest cooperation is maintained with scientists in these organizations.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Basic Studies of the Chemical Composition and Physical Properties of Sugarcane Juice and Its Products. The simpler organic acids that have been determined quantitatively in analyses of numerous samples of sugarcane juice, together with the protein, starch, minerals, and principal sugars, account for at least 95 percent of the juice solids. The methods adapted for these analyses have been employed to obtain information on changes in composition resulting from the lime clarification treatment used industrially. This simple, inexpensive process eliminates most of the protein together with suspended solids and foreign matter, but effects little or no reduction in concentrations of the simpler organic impurities.

Completed analyses of the principal amino acids, and determinations of total nitrogen, in a series of samples of clarified juice and of the raw juice from which each was produced, showed that the standard lime clarification process did not reduce measurably the concentrations of the amino acids in the juice samples. The reduction of 22% to 35% found in total nitrogen content can be attributed almost entirely to precipitation of protein, approximately 80% of which is known to be eliminated in clarification. The concentrations of glutamine were reduced by as much as 50% in juices containing appreciable amounts of this amide, which is known to undergo hydrolysis at temperatures reached in clarification; the more stable asparagine was not altered and concentrations of this amide were higher in most of the clarified juices than in the raw juices from which they were obtained. As there was no significant increase in the concentrations of glutamic acid, hydrolysis of glutamine must lead to formation of pyrrolidone carboxylic acid during clarification. This substance has not been found previously in sugarcane juices, but has been detected in samples of raw sugar.

In other research, samples of both the raw and clarified juice solids from another series of pilot plant processing experiments were analyzed for total and amide nitrogen. Elimination of nitrogen in clarification, largely precipitation of protein, varied from 25% to almost 60% of the total. Samples of juices clarified with added flocculant contained the same percentage of total nitrogen as those of the same juices clarified with lime alone, showing that the flocculant does not affect precipitation of protein. In all experiments but one, the amides accounted for a larger percentage of total nitrogen in clarified than in raw juice. Free amino acids were not eliminated, with or without added flocculant.

Significant progress was made in a concerted investigation of complex organic substances which form an important part of the 5 percent of the total juice solids that have not been completely resolved and identified. Natural, water-soluble gums have been isolated from raw and clarified juices, and from sirups and molasses. Estimated concentrations of 0.5 - 0.7 percent of polysaccharides of this nature in the juice solids would account for major difficulties encountered in clarification and in crystallization of sugar. For characterization purposes, the gums were isolated from molasses in which they are present in higher concentrations (as much as 0.5% of molasses solids) than in juice solids. Preliminary work has shown that two distinct types of material are present in the total gum: one fraction precipitated by 70% alcohol, and another soluble in aqueous alcohol. Glucose, galactose, arabinose, xylose, fructose and rhamnose are present in both fractions. Characterization of the complex gums will make possible the development of quantitative methods for their determination. Such methods are required for development of practical processes to eliminate these impurities which reduce the recovery and impair the quality of raw sugar.

Other complex organic impurities are formed during processing by reactions of sugars and the organic acids; and informal cooperative research with the New York Sugar Trade Laboratory is elucidating their constitution. While these "molasses polymers" are not present in the raw or clarified juices, progress was made in differentiating them from the naturally occurring gums which also accumulate in the molasses as sugar is crystallized.

The trisaccharide, kestose, was isolated and identified from raw sugarcane juice solids, showing it to be a naturally occurring juice constituent. Although earlier workers had found this sugar to be present in molasses and sirups, it was not known whether it occurred naturally in the juice. The concentration of kestose in raw juice solids is about 0.3%. The presence of kestose, together with traces of mannose and psicose detected previously, is important because the presence of these sugars affects the precision of polarimetric determinations of sucrose in the juice. They are also among the constituents that limit the recovery of sugar by crystallization as their relative concentrations increase in the molasses. There is evidence that additional kestose may be formed when the juice and sirups are processed under conditions favoring inversion of sucrose.

Separation of the reducing sugars from sucrose and other reducing substances by partial chromatography on carbon-"Celite" columns, and determination of glucose by a specific enzymatic method, has confirmed the predominance of fructose in the mixture of the sugars present in commercial molasses from various sources. The glucose-fructose ratios ranged from 0.71 to 0.81. The proportions of the two sugars are of the same order as those found in samples of Australian molasses by earlier investigators employing other techniques.

The equivalent reducing power of other reducing substances in molasses has been measured by cuprimetric determinations of the sugars and other substances separated by the carbon column procedure. Identification of the other reducing substances will be necessary to account for the excess reducing power, and its increase during enzymatic inversion for determination of sucrose in molasses. (S5 1-71).

Most of the constituents of the phospholipid fraction of raw sugarcane juice solids have been characterized with the identification of lecithin, the principal constituent of this class, and phosphatidyl-ethanolamine reported previously. Evidence was obtained for the presence of smaller amounts of other phospholipids. The dispersing and emulsifying properties of phospholipids, even when these substances are present in low concentrations, can result in undesirable effects upon clarification, and crystallization of sugar will be affected adversely as they become more concentrated in evaporation of sirup, and in the intermediate molasses.

The research has shown that a relatively small proportion of the total phosphorus in sugarcane juice occurs in the form of complex organic compounds containing phosphorus. The chromatographic techniques that have proven effective for isolating the phospholipids that were identified provide the basis for development of an adequate method to determine the organically combined phosphorus in future research on juice compositions.

B. New and Improved Processing Technology

1. Improved Processing Procedures for Clarifying Sugarcane Juice. The program of pilot-plant research conducted during the cane grinding season at the Audubon Sugar Factory of Louisiana State University was reoriented in the 1960 season to emphasize experimentation on improved methods of clarification of cane juice, while still assisting the industry in carrying out tests to evaluate new canes by the procedures developed in prior years.

Controlled pilot-plant experiments were conducted during the 1960 and 1961 seasons to identify suitable or optimum processing conditions for using the commercial flocculant (Separan AP-30) in clarification of cane juice. This flocculant has become widely used in commercial sugarcane processing, with varying degrees of success. In the 1960 experiments, addition of 2-3 p.p.m. of the flocculant to limed and heated juice, compared with clarification without the flocculant, established the effectiveness of the modified procedure for reducing the quantity of precipitate. An average reduction of about 16% was obtained. A corresponding increase of about 18% in elimination of solids per unit weight of clarifier discharge, and an improvement of 25% in filterability of the clarified juice were found. In the second season's tests, flocculant dosage of 6 p.p.m. based on cane weight was required to increase the filterability of processed juice by 21% and reduce the mud weight to be reprocessed by 27%. Effectiveness of the flocculant in clarification depends on factors such as addition rate, limed juice pH, and soil and phosphate contents of the juice. Cost of the flocculant is a small fraction of the benefits in factory operation to be derived by its use. Exploratory tests employing combinations of bentonite and flocculants to improve clarification gave promising results and will be investigated further.

A second line of work involved standard pilot-plant experiments with juices obtained by promptly grinding cane cut into short pieces by a new

harvester-cleaner combine (Cary), and juices from comparable lots of commercial cane harvested by the conventional mechanical method and cleaned by burning. It was established that the new harvesting method yields juices of improved processing quality. Juice from Cary combined cane contained only one-sixth the amount of soil as the control. In processing, it produced three-fourths the weight of clarifier mud, and contained only one-third the weight of insoluble solids per ton of cane, as compared with the control. Juice from conventionally harvested, burned cane clarified better with less fouling of the juice heaters.

Estimated recoverable sugar per ton of net cane was the same for both harvesting methods. Higher sugar per acre by the conventional method was due to high ground loss with the combine and a slightly higher net cane yield per acre with the conventional method. No difference was observed in the milling of 20-inch pieces and whole-stalk cane.

Details of the harvesting, milling and processing results have been made available to the industry in a comprehensive report prepared jointly with Crops Research Division and the American Sugar Cane League, who cooperated in the research.

Standard pilot plant processing experiments to evaluate new, unreleased varieties of cane were continued in the 1960 and 1961 seasons. Based on the results of the 1960 processing experiments, and other considerations, the Contact Committee of the American Sugar Cane League, which is responsible for authorizing commercial introduction of new varieties, decided not to release any new cane for planting in the 1961 season. The 1961 season tests indicated that unreleased variety C.P. 55-30 is satisfactory in processing characteristics, although it should be tested during a less favorable processing season for comparison. (S5 1-70).

2. Composition of Sugarcane in Relation to Processing. Freeze damaged cane frequently must be processed in Louisiana and Florida, and more complete knowledge of the composition of the juice from such cane is needed to devise means of processing it with minimum losses. To this end, changes resulting from damage caused by natural freezing of cane are being determined by analyses of samples obtained throughout the harvest season, and preserved by lyophilizing. The Crops Research Division, ARS, at Houma, Louisiana, cooperates by providing suitable experimental samples.

In experiments in the 1960 season, high concentrations of aconitic and total carboxylic acids were found in samples of raw juice solids preserved by freeze-drying from cane that was not sufficiently mature for commercial cutting. Samples taken during the harvesting season when the sucrose content had increased contained normal amounts of these acids. There was no significant further change after the cane had been subjected to damage by natural freezing conditions. Determinations of starch confirmed earlier observations that the amounts of this constituent decreased markedly in cane that has been damaged by freezing weather. Changes in total nitrogen, amide and amino acid contents of the samples are being determined. A study of samples collected during the 1961 season is in progress. Included are samples of N. Co. 310 and C.P. 52-68, as well as the C.P. 44-101 used in the similar study in 1960. Analyses of juices from frozen cane will complete the investigation of changes in composition of the non-sugars in such juices which affect their processing quality. (S5 1-71).

3. Applications of Ion-Exchange to Processing of Raw Sugar Sirups in Puerto Rico. This work has been completed with preparation of a detailed report on the investigation of ion-exchange purification of raw sugar sirups; and the project was terminated. Assistance in applying the results to commercial production of liquid sugar in Puerto Rico will continue to be given the sugar refining firm which is cooperating in operation of the pilot plant to obtain additional practical data, while gaining experience needed to design and operate an industrial scale plant. Adoption of granular carbon for decolorizing, in conjunction with the ion-exchange purification process, will ensure production of high grade liquid sugar.

PUBLICATIONS REPORTING RESULTS OF USDA AND COOPERATIVE RESEARCH

Chemical Composition and Physical Properties

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New and Improved Processing Technology

- Coll, E. E., Jackson, J. T. and Guilbeau, W. F. 1961. Separan AP-30 used in pilot plant experiments on sugarcane juice clarification. Sugar Bull. 39, pp. 298-303. Sugar J. 24(11), pp. 34-35, 37.
- Coll, E. E., Guilbeau, W. F., Fort, C. A. and Jackson, J. T. 1962. Standard processing experiments on commercial and unreleased canes during the 1961 Louisiana harvest. Sugar Bull. 40, pp. 181-185.
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AREA NO. 13 - REPLACEMENT CROPS - UTILIZATION POTENTIAL

Problem. Farmers could achieve more economic use of their land if new and profitable crops were available for their choice that would have different end-use patterns from those presently grown. For example, it would be advantageous to develop a new oilseed crop yielding unique fatty acids that could find industrial use in applications for which acids from presently available domestic oilseed crops are unsuitable. To develop a new crop, three basic steps are involved: (1) Survey of wild plants, in cooperation with plant scientists, to identify those having both potentially valuable components and promising agronomic potential for use in the U. S.; (2) detailed physical and chemical characterization of components of interest to obtain clues to likely end uses; (3) selection of the most promising species followed by additional utilization research to explore uses and demonstrate industrial potential and by additional agronomic research to establish proper cultural practices and select the best strains and varieties. Only after these steps have been successfully accomplished can a proposed new crop be offered to agriculture and industry for introduction and development. Obviously, a program of this type is a long-range one. Yet, whether the future of agriculture involves conditions of surplus, of greater emphasis on foods and feeds, or of necessity for greater national self-sufficiency, the nation will benefit from availability of optimum, practical crop plants to serve its needs.

To achieve the objective, survey and characterization work needs to be greatly increased, since the greater the number of species examined, the greater will be the opportunities for finding plants meeting the criteria of high utilization and agronomic potential. Work of the Department has already revealed several promising sources of new potentially valuable water-soluble gums, pulp fibers, and oils containing unique fatty acids such as hydroxy unsaturated acids, capric acid, epoxidized acids and unusual long-chain fatty acids. In order to demonstrate the potential of these new materials, further work is required on their physical and chemical properties and reactions, on processing to obtain maximum recovery from source plants and on byproducts from processing, such as oilseed meals.

USDA PROGRAM

The Department has a continuing long-term program involving organic and analytical chemists engaged at New Orleans, Louisiana in research to develop and evaluate industrial chemical products from the oils of certain new oilseed crops having production potentials as replacement crops. Oils from the seeds of the plants Limnanthes and Cuphea, rich in unusual long-chain unsaturated acids and capric acid, respectively, and from seeds of Umbelliferae such as parsley, carrots, fennel, dill and coriander containing high percentages of petroselinic acid, are currently being investigated. The research is concerned with chemical modification of the oils and their fatty acids to produce materials having potential utility in plastics, plasticizers, synthetic rubbers, protective coatings and other industrial products.

Close cooperation is maintained with the New Crops Research Branch, Crops Research Division, in the procurement of seed and in joint evaluation of the potential of the new crops. The Pharmacology Laboratory of the Western Division, Albany, California, performs tests as needed to determine the

physiological properties of the oils, their derivatives and the meals. Louisiana State University cooperates by testing some of the chemical derivatives for antimicrobial activity. Other appropriate agencies in the Department of Agriculture and the State Agricultural Experiment Stations cooperate by evaluating the utility of some of the new compounds prepared from the oils. Informal cooperation is also maintained with industrial firms for evaluations of promising materials developed in the research.

The Federal scientific effort at the Southern Division devoted to research in this area totals 4.6 professional man-years. All of this effort is on industrial utilization.

During the year a project limited to investigation of the chemical modification of petroselinic acid oils was terminated. A broader line of work, involving Limnanthes, Cuphea and other selected plants, was initiated (under industrial utilization).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

Related programs of State Experiment Stations, and Industry and other organizations, are reported by the Northern Utilization Research and Development Division in Summary of Current Program and Preliminary Report of Progress.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Industrial Utilization

1. Industrial Products from Oilseeds Containing Capric and Unusual Long-Chain Unsaturated Acids. Because of its unique chemical structure, petroselinic acid can be chemically modified to produce derivatives different than those obtainable from the monounsaturated fatty acids of common vegetable oils and animal fats. For example, if petroselinic acid-bearing oilseeds can be developed as economic crops, petroselinic acid can be used as a chemical source of adipic acid, which has an estimated current established market of 400 million lbs. annually and lauric acid presently prepared from imported coconut oil in annual volume of over 100 million lbs. In continued research on petroselinic acid, a number of additional chemical derivatives have been prepared which may have industrial utility.

Formoxylation of petroselinic acid yielded on hydrolysis 5-, 6-, 7-, and 8-hydroxystearic acids. A mixture of the 6- and 7-hydroxystearic acids was produced in good yield by hydrogenation of 6,7-epoxystearic acid. These hydroxy acids could be useful as components of polyester resins for plastics and coatings.

By reaction of urea or ammonia with petroselinic acid, petroselinamide has been prepared. Conditions were established for reacting petroselinic acid with ammonia to produce petroselinonitrile, and reducing the nitrile to petroselinyllamine. A method has also been devised for preparing petroselinonitrile in good yield (70%) from crude parsley seed oil triglyceride, a more economically feasible starting material than pure petroselinic acid. Some of these nitrogen-containing organic compounds possess interesting surface active and antimicrobial properties. Petroselinic acid has been found to be a better antimicrobial agent than oleic acid, and petroselinyllamine derivatives are very effective in inhibiting growth of some microorganisms.

Lauryl alcohol and ethyl hydroxycaproate have been prepared in good yields by application of sodium borohydride reduction to the ozonide of ethyl petroselinate. Using another approach, catalytic hydrogenation, conditions have been found which result in fairly good conversion of the ozonolysis products from ethyl petroselinate to lauryl alcohol and ethyl hydroxycaproate. Procedures were also developed for preparation of laurylamine and aminocaproic acid from the ozonolysis product of petroselinic acid. Hydroxycaproic acid and aminocaproic acid can be converted into useful polymers of the polyester and polyamide types, respectively.

Research was initiated on the oils from Limnanthes douglasii and Cuphea seed. A pilot-plant extraction of 100 lbs. of the former seed was made, and isolation of 5-eicosenoic acid from the oil is in progress. Attempts to modify starch by reaction with capric acid, the principal acid of Cuphea seed oil, to impart flexibility to films of adhesive starches were not very promising. However, chemical modification of capric acid should yield derivatives having antimicrobial, insecticidal, and other types of biological activity, as well as chemicals for use in applications where surface activity and related physical properties would be important. Studies of the chemical modification of the various fatty acids will continue. (S5 5-38; S5 5-45).

PUBLICATIONS REPORTING RESULTS OF USDA AND COOPERATIVE RESEARCH

Industrial Utilization

- Dupuy, Harold P., Goldblatt, Leo A. and Magne, Frank C. February 14, 1961. Polymeric composition containing fatty acid derivative or morpholine. U.S. Patent No. 2,971,855.
- Fore, Sara P., Holmes, Raiford L. and Bickford, W. G. 1960. Preparation of petroselinic acid. J. Am. Oil Chemists' Soc. 37, pp. 490-491.
- Fore, Sara P., Pastor, H. P., Hughes, J. P. and Bickford, W. G. 1960. Derivatives of Jojoba oil as plasticizers for vinyl polymers and Buna-N rubber. J. Am. Oil Chemists' Soc. 37, pp. 387-390.
- Fore, Sara P. and Bickford, W. G. 1961. Catalytic hydrogenation of cis-6,7-epoxyoctadecanoic acid. J. Org. Chem. 26, pp. 2104-2105.
- Novak, Arthur F., Clark, Gladys C. (LSU, Baton Rouge, La.) and Dupuy, Harold P. 1961. Antimicrobial activity of some ricinoleic and oleic acid derivatives. J. Am. Oil Chemists' Soc. 38, pp. 321-324.
- Placek, Lida L. and Bickford W. G. 1961. Positional isomerism in the formoxylation of petroselinic acid. J. Org. Chem. 26, pp. 864-866.

AREA NO. 14 - RICE PROCESSING AND PRODUCTS

Problem. The productive capacity of U. S. rice growers has increased faster than domestic and export consumption over the past decade, thus limiting the income potentially available from this major world food grain. Detailed knowledge of chemical composition and physical properties, as related to processing is needed to guide milling, processing and product development of U. S. rices so that they can better meet the quality and new product requirements needed for expanded markets. New and diverse food products from rice that are easy to prepare, have flavor and texture appeal, and are economical to manufacture, are needed to increase the total consumption of rice both domestically and abroad.

USDA PROGRAM

The Department has a continuing long-term program involving at New Orleans, Louisiana, biochemists and analytical chemists engaged in basic and exploratory studies on the chemical and physical changes undergone by rice constituents during aging of rice after harvest, which will account for the improvement in cooking characteristics observed after storage of milled rice for a few months. Present research involves investigations of the biochemical characteristics of rice as affected by and in relation to aging and processing characteristics, with special emphasis on the susceptibility of rice starch to amylolytic action.

Close cooperation is maintained, under formal memoranda of understanding with the Louisiana, Arkansas and Texas Rice Experiment Stations, who supply rice samples of known variety and cultural history for the experimental studies. The Rice Inspection Service, Grain Division, AMS, New Orleans, Louisiana, cooperates by providing assistance in milling and grading the rice samples used in the research investigations.

The Federal scientific effort at the Southern Division devoted to research in this area totals 2.6 professional man-years. All of the present effort is on chemical composition and physical properties.

During the year a broad project on investigation of chemical and physical changes occurring in Southern grown rice during aging was terminated. The research has been redirected toward the specific investigation of the intrinsic amylases in the rice kernel and the susceptibility of the rice starches to external amylases (under chemical composition and physical properties).

RELATED PROGRAMS OF STATE EXPERIMENT STATIONS AND INDUSTRY

Related programs of State Experiment Stations and Industry and other organizations, are reported by the Western Utilization Research and Development Division in Summary of Current Program and Preliminary Report of Progress.

REPORT OF PROGRESS FOR USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Studies of Chemical and Physical Changes in Rice as Affected by Aging and Processing. Research on the gas plasma irradiation of rice was conducted in cooperation with the Agricultural Engineers, ARS, because there seemed to be a possibility that this treatment might be useful in developing instant rice products. This work was terminated on the completion of experiments on treatment of rice bran and hulls. Irradiation caused these components to become much more susceptible to water penetration. It altered the oil in the bran, with inhibition of free fatty acid formation, and increased the viscosity and decreased the solubility of the oil in fat solvents. It was concluded that polymerization and reduction in the degree of unsaturation are responsible for these effects. The process could result in a controlled modification of vegetable oils by irradiation of the extracted oils, or possibly of the oil-bearing seeds, with resultant products of industrial or scientific significance. For modifying whole milled rice a combination of heat and vacuum proved to be the causative agent rather than the gas plasma radiation. The heat and vacuum treatment reduced the cooking time of the whole milled rice by 50%, increased the cooked grain size and maintained or improved the edible characteristics of the cooked rice. Although the heat-vacuum processed products offer interesting possibilities as "instant" rice products, they lack certain essential convenience features; for example, pre-soaking is required. At the present time neither gas plasma irradiation nor the heat-vacuum treatment appear attractive for the preparation of instant or quick-cooking rice products.

The variations in the chemical and physical composition of rice during aging have been studied to elucidate the mechanism through which the beneficial changes occurring during aging take place. Many of the characteristics of rice important to the competitive position of rice in the various marketing areas will be controllable once the compositional factors determining the desired characteristics are known.

In current research the effects of aging of rice at ambient temperature and at 40° F. on its chemical and physical properties have shown that the progressive changes during aging result in an improvement in the organoleptic characteristics of the cooked rice (i.e., texture, appearance, cohesiveness). Changes in these characteristics closely parallel changes in hydration and viscometric properties. The progressive improvement in organoleptic characteristics is also accompanied by well defined changes in native amylase activity and changes in the susceptibility of the rice starch to introduced amylases. Bluebonnet-50 rice has not exhibited any significant change in chemical composition, i.e., starch, protein, sugars, etc., for a 9-month aging period.

Although a definitive knowledge of the exploratory mechanism whereby the aging changes occur has not been obtained in this exploratory study, the correlation of changes in physical properties (hydration and posting properties) with changes in organoleptic characteristics leading to improvement of the culinary quality of aged rice represents a distinct advancement in the knowledge of the aging process. The fact that the gross chemical composition of rices remained almost constant during aging suggests that the difference between fresh and aged rice may be due to more subtle changes in the nature

and quality of the rice constituents (rice starch, for example) rather than their composition (Si 4-11).

PUBLICATIONS REPORTING RESULTS OF USDA AND COOPERATIVE RESEARCH

Chemical Composition and Physical Properties

- Anon. 1960. Proceedings of Conference on Utilization of Rice, March 7-9, 1960, New Orleans, La. (Sponsored jointly by Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, La. and The Rice Millers' Association, New Orleans, La.) 27 pp.
- Deobald, Harold J. 1961. Study on rice by Southern Laboratory - SURDD reports rice research progress 1960-61. Rice J. 64(7), pp. 58-59.
- Hogan, Joseph T. and Deobald, Harold J. 1961. Note on a method of determining the degree of milling of whole milled rice. Cereal Chem. 38, pp. 291-293.
- Hogan, J. T. and Roseman, A. S. 1961. Gas plasma irradiation of rice. II. Effect of heat on hydration and cooking characteristics. Cereal Chem. 38(5), pp. 432-438.
- Roseman, A. S., Hogan, J. T. (Southern Utilization Research and Development Division) and Stone, R. B. and Webb, J. C. (Agr. Eng. Res. Div., USDA, Univ. of Tenn.). 1961. Gas plasma irradiation of rice. I. Hydration characteristics. Cereal Chem. 38(5), pp. 423-432.

New and Improved Processing Technology

- Pominski, J. (SURDD), Wasserman, T. (WURDD), Schultz, E. F., Jr. (Biometrical Services, ARS), and Spadaro, J. J. (SURDD). 1961. Increasing laboratory head and total yields of rough rice by milling at low moisture levels. Effects of Bluebonnet-50---a long-grain variety. Rice J. 64(10), pp. 11-15.
- Pominski, J. (Southern Utilization Research and Development Division), Wasserman, T. (Western Utilization Research and Development Division, Spadaro, J. J. and Decossas, K. M. (Southern Utilization Research and Development Division) and Doré, A. B., Jr. (Doré Rice Mill, Crowley, La.). 1961. Improvements in commercial drying of Southern-grown rice I. Zenith-A medium-grain variety. Rice J. 64(9), pp. 10, 12-13, 16-17.

Line Project Check List -- Reporting Year July 1, 1961 to June 30, 1962

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in	
			Summary of Progress	Area & Subheading
S1 4-	Rice Utilization Investigations - Southern Region			
S1 4- 11**	Investigation of the chemical and physical changes occurring in Southern grown rice during aging to determine the constituent changes affecting the processing characteristics	New Orleans, La.	Yes	14-A-1
S2 1-	Cotton Utilization Investigations			
S2 1- 130**	Development of an accelerated spinning ends down test for rapidly evaluating the processing efficiency of cotton	New Orleans, La.	Yes	2-B-3
S2 1- 132**	Development of winter-weight cotton fabrics on the cotton processing system that will successfully compete with fabrics made from synthetic fibers and blends of synthetic fibers for clothing and household use	New Orleans, La.	Yes	5-E-1
S2 1-133 (C)**	Development of apparatus and methods for automatically preparing cotton fiber specimens suitable for scanning and rapidly obtaining accurate fiber-length and length-distribution measurements as aids to more efficient utilization of cotton	Hoboken, N. J.	Yes	2-B-1
S2 1-137	Improved cleaning at the cotton card	New Orleans, La.	Yes	3-A-3
S2 1- 138**	Research to improve the light and weathering resistance of flame-resistant cotton products	New Orleans, La.	Yes	5-D-1
S2 1-140 (C)	Development of improved winter-weight cotton fabrics on the woolen processing system that will successfully compete with fabrics made from synthetic fibers and blends of synthetic fibers for clothing and household use	Lowell, Mass.	Yes	5-E-1
S2 1-143 (C)**	Enhancement of cotton's competitive position through the development of elastic cotton yarns for socks and other commercial applications	Clemson, S. C.	Yes	5-E-1
S2 1-148 (C)	Investigations designed to develop reactive finishing agents for cotton that will provide improved elastic and strength properties by the introduction of cellulose crosslinks of optimum size and structure	Lowell, Mass.	Yes	4-A-2
S2 1- 149**	A study of the influence of cotton fiber properties and atmospheric conditions on nep formation to provide a basis for selecting cottons of improved processing efficiency and increased utilization	New Orleans, La.	No	
S2 1- 150**	Role of catalysts in the mechanism of the reactions of wash-wear resins with cotton	New Orleans, La.	Yes	4-A-1
S2 1-151	A study of the etherification of cellulose using radioactively labeled etherifying reagents to contribute basic information on wash-wear cottons	New Orleans, La.	Yes	1-A-1
S2 1-152	A microscopical study of degradation of cotton cellulose structure by various agents	New Orleans, La.	Yes	1-A-4
S2 1-153	Determination of the effect of the principal types of spotted cotton on product quality and processing efficiency to obtain optimum use of such cotton	New Orleans, La.	Yes	2-A-1
S2 1-154	Development of a Bale-Breaker-Blender for opening and blending cotton	New Orleans, La.	Yes	3-A-1
S2 1- 155**	Evaluation of the physical properties of cotton chemically or physically treated to enhance their wash-and-wear values	New Orleans, La.	Yes	4-A-1
S2 1-156	Development of weather- and rot-resistant cotton fabrics	New Orleans, La.	Yes	5-A-1
S2 1-157 (C)	Design and development of acceptable cotton crepe apparel fabrics to compete with synthetic fibers in these markets	Philadelphia, Pa.	Yes	5-F-1

** Terminated

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
S2 1-158 (C)**	Systematic investigation of non-aqueous swelling agents for cellulose to provide new chemical and physical modifications of cotton	Princeton, N. J.	Yes	1-B-1
S2 1-159**	Treatment of cotton with gamma radiation and chemicals to develop improved cotton products	New Orleans, La.	Yes	1-B-2
S2 1-160**	Investigation of the effect of fiber drag on the draftability of cottons to improve the processing techniques and quality of yarns	New Orleans, La.	Yes	1-A-6
S2 1-161	Crosslinking of cotton cellulose with difunctional etherifying agents using alkaline catalysts	New Orleans, La.	Yes	1-B-1
S2 1-162	Development of wash-wear cotton fabrics and garments with durable creases and shape holding properties	New Orleans, La.	Yes	4-C-1
S2 1-163	Development of optimal structures for cotton fabrics for wash-wear products	New Orleans, La.	Yes	4-B-3
S2 1-164	Development of a machine for removing short fibers from cotton	New Orleans, La.	Yes	3-A-4
S2 1-165	Study of the infrared absorption spectra of native, degraded and chemically modified cotton cellulose as a means of elucidation of structural and chemical changes due to chemical treatment	New Orleans, La.	Yes	1-A-5
S2 1-166	Development of wash-wear cotton fabric by reaction with improved formaldehyde	New Orleans, La.	Yes	4-B-1
S2 1-167	Systematic exploratory investigation of chemical pretreatments as a means of producing resilient cotton fabrics having improved abrasion and tear resistance	New Orleans, La.	Yes	1-B-1
S2 1-168	Exploration of cellulosic crosslinks capable of being broken and reformed at will	New Orleans, La.	Yes	1-B-1
S2 1-169	A study of the reaction of cotton with epoxy compounds in the presence of free radicals or disproportionating products	New Orleans, La.	Yes	1-B-1
S2 1-170 (C)	Investigation of the relationships between ease-of-care performance and the geometry of cotton fabrics	Dedham, Mass.	Yes	4-B-3
S2 1-171	Application of crosslinking treatments to chemically modified cottons	New Orleans, La.	Yes	4-B-2
S2 1-172	Exploratory study of means of producing thermoplastic cottons	New Orleans, La.	Yes	1-B-1
S2 1-173 (C)	Determination of the mechanics of nep formation in cotton during textile mechanical processing	Cambridge, Mass.	Yes	1-B-4
S2 1-174	Microscopical investigation of reaction products in chemical modifications of cotton fibers	New Orleans, La.	Yes	1-A-3
S2 1-175 (C)	Fundamental investigation of the effects of specific type finishes on soiling of and soil removal from cotton	Washington, D.C.	Yes	5-C-1
S2 1-176*	Preparation of cotton products containing radiation-induced polymers having desirable physical properties	New Orleans, La.	Yes	1-B-2
S2 1-177	N-methylol finishes for high quality durable wash-wear cotton fabrics	New Orleans, La.	Yes	4-A-2
S2 1-178(C)*	Large-scale spinning evaluation of the effect of fiber properties and spinning variables on yarn properties and end breakage during spinning	Auburn, Ala.	Yes	2-A-1
S2 1-179*	Development of optimum processing procedures to minimize the detrimental effects of short fibers in cotton spinning performances and product quality	New Orleans, La.	Yes	2-A-2
S2 1-180*	Modification of cotton with fluorochemicals to impart durable water and oil repellency	New Orleans, La.	Yes	5-C-1

* Initiated
** Terminated

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in	
			Summary of Progress	Area & Subheading
S2 1-181*	Improvement in the bulk resilience and cohesion of cotton batts as a means of enhancing cotton's competitive position in this market	New Orleans, La.	Yes	5-E-3
S2 1-182*	Evaluation of the swelling behavior of cotton fibers in various environments by observation of the untwisting of single yarns	New Orleans, La.	Yes	1-A-2
S2 1-183 (C)*	Investigation of the effects of mechanical treatments prior to, during, and following resin finishing on the ease-of-care properties of fabrics and garments	Raleigh, N. C.	No	
S2 1-184*	An engineering study of the feasibility and practicality of chemical and/or resin treatment of roving by continuous processing as an intermediate step in the mechanical processing of cotton	New Orleans, La.	Yes	5-F-1
S2 1-185*	Basic investigations to characterize fiber damage in mechanical processing from opening through carding to provide information needed to develop improved textile machinery and processing methods	New Orleans, La.	Yes	2-A-2
S2 1-186*	Chemical attachment of reactive compounds to cotton cellulose by means of polyfunctional reagents	New Orleans, La.	Yes	1-B-1
S2 1-187*	The development of stretchable cotton fabrics for various outdoor uses by slack mercerization	New Orleans, La.	Yes	5-E-2
S2 1-188*	A fundamental investigation of the drying of chemically modified cotton, with emphasis on resin treated cotton, as a means of producing cotton products of superior quality	New Orleans, La.	Yes	1-B-4
S2 1-189*	Investigation of wet and dry crease recovery mechanisms in wash-wear cotton products	New Orleans, La.	Yes	4-A-1
S2 1-190*	Exploratory investigations to impart improved properties to cotton needed for specific end uses	New Orleans, La.	Yes	5-D-2
S2 1-191*	Investigation of various finishes with respect to soiling and soil removal from cotton	New Orleans, La.	Yes	5-C-1
S2 1-193*	Development of stretchable-type cotton yarns and fabrics that will successfully compete with fabrics made from synthetic fibers and blends of synthetic fibers for clothing, household and industrial uses	New Orleans, La.	Yes	5-E-1
S2 1-194*	Exploratory investigation of methods for imparting durable luster and related appearance characteristics to cotton textiles	New Orleans, La.	No	
S3 2-	Citrus and Other Fruit Utilization Investigations - Southern Region			
S3 2-23	Investigations to develop new and improved processed products from selected minor fruits, with emphasis on avocados, limes and Meyer lemons	Weslaco, Texas	Yes	9-B-4
S3 2-28**	Studies on the chemistry and the mechanism of formation of oxidized flavors in citrus products	Winter Haven, Fla.	Yes	9-A-1
S3 2-30**	Investigations of linalool, terpineol, flavonoid constituents and similar materials in oranges, and their influence on the properties of processed orange products	Winter Haven, Fla.	Yes	9-A-2
S3 2-32	Investigations on the "foam-mat" drying of concentrated citrus juices to provide new citrus products of optimum flavor and high stability	Winter Haven, Fla.	Yes	9-C-1

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Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
S3 2-33	Investigations to develop a highly colored frozen concentrated juice and grapefruit drinks from colored grapefruit by pulp fortification	Weslaco, Texas	Yes	9-B-3
S3 2-34	Investigation of the origin of carotenoid precursors and the biochemical mechanism of their conversion to carotenoids in grapefruit as a basis for improvement of processing characteristics of and products from colored grapefruit	Weslaco, Texas	Yes	9-A-4
S3 2-35	Investigations on preservation of chilled citrus products to prevent spoilage and permit delivery of improved products	Winter Haven, Fla.	Yes	9-B-1
S3 2-36*	Investigations on composition of essential citrus oil as related to flavor of juices, concentrates, powdered juice and other products, with special emphasis on essential orange oil	Winter Haven, Fla.	Yes	9-A-1
S3 2-37*	Investigations of the neutral fraction of orange peel extract for the isolation of bitter principles	Winter Haven, Fla.	Yes	9-A-2
S3 2-38*	Investigation of the chemical nature and physical state of components of cloud of orange juice, with a view to better understanding and control of factors affecting stability of frozen concentrated orange juice	Winter Haven, Fla.	Yes	9-A-3
S3 5-	Sweetpotatoes, Cucumbers and Other Vegetable Utilization Investigations - Southern Region			
S3 5-16	Investigations to develop new and improved processed products from vegetables with emphasis on cucumbers, snapbeans, southern peas, tomatoes and spinach	Raleigh, N. C.	Yes	10-C-2
S3 5-17	Investigations to develop improved processed products from celery with emphasis on flavor components	Weslaco, Texas		10-B-2
S3 5-18**	Investigation of the influence of naturally occurring "plant" enzyme inhibitors, irradiation, brine strength (% salt) and other processing variables in improving processed cucumber products	Winter Haven, Fla.	Yes	10-A-1
S3 5-19	Development of a practical pilot plant for precooked dehydrated sweetpotato flake products, with improved product quality and processing efficiency to extend the utilization of sweetpotatoes	Raleigh, N. C.	Yes	10-C-2
S3 5-20*	Investigation of methods for the controlled fermentation of cucumbers with emphasis on the application of pure culture techniques to reduce processing costs and improve product characteristics	New Orleans, La.	Yes	10-B-1 10-C-1
S4 1-	Cottonseed, Peanut and Other Oilseed Investigations - Southern Region	Raleigh, N. C.	Yes	10-C-2
S4 1-73 (C)**	Investigations of the reactions of gossypol to aid the development of improved cottonseed meal and oil of enhanced value	Knoxville, Tenn.	Yes	6-A-2
S4 1-78 (C)**	Applications research on vehicles and surface coatings containing derivatives of tung oil, castor oil or pine gum	Gainesville, Fla.	Yes	8-B-2
S4 1-81 (C)**	Preparation of intermediates for making elastomers, plastics and protective coatings from chemicals derived from Southern grown agricultural commodities	Oxford, Miss.	No	
S4 1-84**	Development of new hydrogenation techniques for cottonseed and peanut oils to produce improved edible fat products and intermediates for inedible, industrial use	New Orleans, La.	Yes	6-B-2

* Initiated
** Terminated

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
S4 1-87**	Investigations to isolate, identify and measure chemical constituents in peanuts which contribute to quality of processed peanut products	New Orleans, La.	Yes	7-A-2
S4 1-88	Investigations of solubilities of long-chain fatty acids and their derivatives important to research and industrial utilization of fatty acids from vegetable oils of Southern Region	New Orleans, La.	Yes	6-A-3
S4 1-89(C)	Polymerization of vegetable oil, pine gum and sugarcane derivatives and evaluation of properties of the polymers for use as elastomers, plastics, thickening agents and protective coatings	Tucson, Arizona	Yes	6-D-1 11-B-3
S4 1-90	New polyester products from cottonseed oil for use as edible and inedible coating materials, waxes, resins, plasticizers and lubricants	New Orleans, La.	Yes	6-B-1
S4 1-91	Preparation of new and improved confectionery fats and oils from cottonseed and peanut oils	New Orleans, La.	Yes	6-B-1
S4 1-92	Pilot-plant scale development of a process for improving cottonseed oil color based on highly active adsorbents	New Orleans, La.	Yes	6-B-2
S4 1-93	Chemical modification of tung oil and its fatty acids to produce materials having utility as protective coatings, agricultural chemicals, surfactants or plasticizers	New Orleans, La.	Yes	8-B-2
S4 1-94	Pilot-plant investigations of cottonseed processing using a hexane-acetone-water solvent mixture to improve meal and oil quality	New Orleans, La.	Yes	6-C-2
S4 1-95	Development of new information basic to the production of cottonseed meals that can be fed to swine and poultry without restriction	New Orleans, La.	Yes	6-C-1,2
S4 1-96	Investigations on the improvement of the color and quality of off-colored cottonseed oils	New Orleans, La.	Yes	6-A-2,3
S4 1-97	Investigation of physiologically active constituents in cottonseed meal that affect the utilization of the meal as a protein supplement in nonruminant feeding	New Orleans, La.	Yes	6-C-1
S4 1-98	Development of exterior intumescent fire-retardant surface coatings from tung oil alkyds	New Orleans, La.	Yes	8-B-1
S4 1-99	Investigation of long chain fatty amides and derivatives potentially useful as plasticizers, polyurethane foams and other industrial uses	New Orleans, La.	Yes	6-D-1
S4 1-100*	Investigations of the constituents and their modifications by processing that influence nutritive properties and consumer acceptance of processed peanut products	New Orleans, La.	Yes	7-A-2
S4 1-101*	Engineering studies to develop a commercial process for preparing cocoa butter-like fat from cottonseed oils	New Orleans, La.	Yes	6-B-2
S4 1-102*	Development of hydrogenation techniques which will produce the least possible isomerization in edible fat products prepared from cottonseed oil and peanut oil	New Orleans, La.	Yes	6-B-2
S4 1-103 (C)*	Investigations of gossypol esters and of mild oxidation products of gossypol and gossypol derivatives to develop information needed to aid the production of cottonseed meals and oils of the highest quality	Knoxville, Tenn.	Yes	6-A-2
S4 1-104 (C)*	Investigation of the chemical and physical properties of cyclopropene fatty acids in cottonseed	Urbana, Ill.	Yes	6-A-2

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Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
S5 1-	Sugars and Sirups Investigations - Southern Region			
S5 1-70	Pilot-plant development of new and improved methods of clarification and processing to increase the recovery and improve the quality of raw cane sugar	New Orleans, La. Baton Rouge, La.	Yes	12-B-1
S5 1-71	Investigation of the composition of sugarcane in relation to processing efficiency	New Orleans, La. Houma, La.	Yes	12-A-1 12-B-2
S5 2-	Naval Stores Investigations - Southern Region			
S5 2-31**	Development of industrial chemicals, plastics, elastomers, plasticizers, surface coatings, resins and lubricating oil additives by isomerization and low temperature polymerization of pine gum and rosin and resin acids derived from pine gum with ionic type catalysts	Olustee, Fla.	No	
S5 2-32**	Investigation of processes for the conversion of pine gum to rosin and resin acid composition having a high levopimaric acid content	Olustee, Fla.	Yes	11-C-1
S5 2-33**	Development of industrial chemicals for such fields as plastics, plasticizers and surface coatings by conversion of selected resin acids derived from pine gum and gum rosin into polyfunctional compounds such as dibasic acids, amino acids, and hydroxyl acids by reacting the resin acids with chemicals to introduce other functional groups	Olustee, Fla.	Yes	11-B-3
S5 2-34**	Synthesis of resins, plasticizers and other potentially useful chemicals by condensing pine gum and its components with reactive dieneophiles	Olustee, Fla.	Yes	11-B-3
S5 2-36	The isolation and characterization of some of the major unidentified components in pine gum, rosin and some of their derivatives	Olustee, Fla.	Yes	11-A-1
S5 2-37	The photochemical addition of suitable reagents to resin acids of pine gum origin to produce new chemicals of potential utility in the fields of surface active agents, textiles, paper and plastics	Olustee, Fla.	Yes	11-B-2
S5 2-38	Preparation of chemical intermediates from pine gum products for use in the preparation of new synthetic polymers, plastics and resins to expand the utilization of turpentine and rosin	Olustee, Fla.	Yes	11-B-1
S5 2-39	Development of a method for the determination of rosin and rosin derivatives in protective coatings	Olustee, Fla.	Yes	11-B-3
S5 2-40	Production of reactive chemical intermediates from turpentine by reaction with selected low molecular weight reagents	Olustee, Fla.	Yes	11-B-1
S5 2-41*	Development of process for isolation of levopimaric acid from pine gum	Olustee, Fla.	Yes	11-C-1
S5 2-42*	Polyester resins from pine gum derivatives	Olustee, Fla.	Yes	11-B-3
S5 2-43*	The preparation of polyfunctional compounds from rosin, resin acids and resin acid derivatives through their reaction with formaldehyde	Olustee, Fla.	Yes	11-B-3
S5 5-	New and Replacement Crops Utilization Investigations - Southern Region			
S5 5-38**	Investigation of chemical modification of petroselinic acid oils to produce materials having utility in plastics, synthetic rubbers, protective coatings and other industrial products	New Orleans, La.	Yes	13-A-1

* Initiated

** Terminated

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
S5 5-45*	Investigation on chemical modification of oils from potential new oilseed crops such as <u>Limnanthes</u> and <u>Cuphea</u> to produce materials having utility in plastics, plasticizers, synthetic rubbers, protective coatings and other industrial products	New Orleans, La.	Yes	13-A-1
SG-0-1***	Development of Emulsifiable Oils and Fats For Use in Intravenous Alimentation, for the Office of the Surgeon General -- Southern Region	New Orleans, La.	Yes	6-A-2 6-B-1
UR-A7-(40)-3*	A study of the relationship of substituent fatty acid groups on the physical properties of diacid triglycerides of palmitic and stearic acids as a means of increasing the utilization of cottonseed oil for food and industrial purposes	Bombay, India	No	
UR-A7-(20)-4*	Investigation of the photochemical degradation of cotton to derive information which would enhance the utilization of cotton	Bombay, India	No	
UR-A10-(20)-4	A fundamental study of oxidation of cotton by hypochlorite, hypobromite, hypoiodite and other oxidizing agents to obtain data on kinetics of oxidation and changes in physical and chemical properties, as a contribution to improved uses for cotton	Jerusalem, Israel	Yes	1-B-3
UR-A10-(20)-5	Fundamental investigation of crimp in cotton fibers and its relationship to other fiber properties, as well as its effect on processing performance and product quality	Jerusalem, Israel	Yes	1-A-6
UR-E9-(00)-29	Investigation of preparation and properties of alkyl aryl ketones and their derivatives from vegetable oils and animal fats to provide information of potential value in increasing utilization of these commodities in such industrial products as surface-active agents, lubricants, plasticizers and fungicides	Paris, France	Yes	6-D-1
UR-E9-(20)-61	A fundamental study of the relation of crystallinity to accessibility in native and modified cotton, to obtain information on the super-molecular structure of cotton that is needed in the development of improved cotton products	Paris, France	Yes	1-A-5
UR-E10-(20)-2*	Development of an apparatus for counting neps in cotton card web as an aid toward increasing the quality of cotton products	Reutlingen-Stuttgart, West Germany	No	
UR-E19-(20)-4*	A fundamental study of the role of the structural elements of the cotton fiber in response to stress in deformation and recovery, to obtain information needed in the development of improved cotton products	Delft, Holland	No	
UR-E25-(20)-1	Development of methods and equipment for determining irregularity of transparency of card web and for counting of neps, by means of electronic devices, as aids to improving product quality in cotton textile operations	Barcelona, Spain	Yes	2-B-2
UR-E25-(20)-2	Determination of relationship between the cohesion of cotton fibers and other physical properties of fibers, rovings, and yarns, as a step in improving product quality and processing efficiency	Barcelona, Spain	Yes	2-A-1

* Initiated

*** There are no line projects under this work project

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj.	Incl. in
			Summary of Progress	Area & Subheading
UR-E25- (20)-13	Determination of effect of drafting forces in high-draft systems on uniformity and strength of cotton yarns as a step in improving product quality and processing efficiency	Barcelona, Spain	Yes	2-A-2
UR-E26- (20)-2*	Fundamental investigation of setting reactions for cotton fabrics and garments, to develop information basic to the improvement of cotton products, thereby increasing the utilization of cotton	Göteborg, Sweden	No	
UR-E29- (20)-4	Fundamental investigation of the causes of warp breakage in the weaving of cotton yarns, as a basis for improving quality and reducing costs of production	Didsbury, Manchester, England	Yes	2-A-1
UR-E29- (20)-6	Fundamental study of the microbiological breakdown of natural cotton fiber, as a contribution to the better preservation of cotton products	Didsbury, Manchester, England	Yes	1-A-4
UR-E29- (20)-9	Fundamental study of the pyrolysis of cotton cellulose to provide information needed for improvement of flame-resistant treatments for cotton	Didsbury, Manchester, England	Yes	1-B-3
UR-E29- (40)-26	Studies on the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components, to obtain fundamental information that will contribute to the development of improved edible products and hence to expanded utilization of cottonseed oil	Leatherhead, Surrey, England	Yes	6-A-3
UR-E29- (20)-35	Fundamental investigation of preparation and properties of esters, anhydrides, hydrazides, pseudohalides, fluorides and related compounds of the phosphonitrilic chlorides for use in preparing new products to increase the utilization of cotton	London, England	Yes	1-B-1
UR-S9- (40)-2	Preparation, characterization and evaluation of derivatives of gossypol from cottonseed for use as biologically active materials, ultra-violet absorbers and other valuable products	Montevideo, Uruguay	Yes	6-D-1

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